Electrostatic Lattice Energy of $PbSO_4$, $BaSO_4$, $SrSO_4$ and $CaSO_4$(1)

By Yosio SAKAMOTO

(Received March 1, 1952)

§ 1. Lattice-Energy Problem on the Complex Ionic Crystal

The lattice energy of ionic crystals of simple composition and structure has been studied fairly completely, though this subject still leaves room for more thorough consideration at least in some particular aspects, for instance, in the strict application of thermodynamics. On the contrary, few researches have been made into ionic crystals of so complex a structure that the degree of their symmetry is small or their atoms form into partial groupings. One of the chief purposes of the author is to study these complex ionic crystals, especially to elucidate(2) physicochemical properties of radical ions, the properties not a few of which (e. g., the energies fo hydration) have remained quite obscure.

Among the ionic crystals whose lattice energies have so far been evaluated by means of computing lattice sums,(3) those which belong to the rhombic system have the smallest degree of symmetry. No more than two studies(4)(5) have been made on these rhombic crystals, which, moreover, contain radical ions. In the one case,(4) however, the treatment seems to be unsatisfactory, and in the latter(5) the spatial arrangement of the ions is orderly enough.

On the other hand, the ionic arrangement in the rhombic crystals of lead sulfate, in which Dr. Kobayashi(2) was interested, and of the alkaline earth sulfates is relatively irregular and complex. So, first, for the rectangular crystal lattice of any complexity a set of expressions of Madelung's coefficient(6) is derived, and then verified in two simple cases by means of numerical application. The mode of calculation based on this set of expressions will produce effectually an exact and precise result with minimum effort, even for the cases considerably complicated.

§ 2. A Set of Expressions for the Calculation of Madelung's Coefficient M_d

2.1) The crystal lattice in general.(7)—The electrostatic potential energy per mol., $\varPhi_1$, of a crystal lattice is expressed by

$$\varPhi_1 = -Ne^2M_d/d \tag{1}$$

where d is a quantity proportional to length and M_d Madelung's coefficient(6) referred to d. M_d may be represented, through Ewald's method,(8) by a set of expressions suitable for the calculation of its value, thus:

$$\begin{aligned}
&M_d = -\{(d/\delta)^3L/\pi + \bar{Y} + Y/s - \varepsilon d/\sqrt{\pi}\}\sum_h z_h^2;\\
&L = \mathop{S'}_{\bar{l}} w_l L_l,\ L_l = e^{-\kappa\lambda_l}/\lambda_l,\ \kappa = (\pi/\varepsilon d)^2,\\
&\lambda_1 = |\vec{q}^{\,1}d/2\pi|^2,\ w_l = 1 + (2/s)X_l,\\
&X_l = (\nu/\sum_h z_h^2)\sum_{(kk')}{}' z_k z_{k'} \cos(\vec{q}^{\,l}\vec{r}_{kk'});\\
&\bar{Y} = \mathop{S'}_{\bar{l}} \bar{Y}_l,\ \bar{Y}_l = G(\varepsilon d\bar{\eta}_l)/\bar{\eta}_l,\ \bar{\eta} = |\vec{r}^{\,l}|/d;\\
&Y = (\nu/\sum_h z_h^2)\mathop{S}_{l}\sum_{(kk')}{}' z_k z_{k'} \overset{l}{Y}_{kk'},\\
&\overset{l}{Y}_{kk'} = G(\varepsilon d\overset{l}{\eta}_{kk'})/\overset{l}{\eta}_{kk'},\ \overset{l}{\eta}_{kk'} = |\vec{r}^{\,l}_{kk'}|/d;\\
&s = \sum_k 1 = \sigma\sum_h 1 = \sigma\nu,\ h = 1, 2, \cdots\cdots\nu;\\
&\bar{l} = (\bar{l}_1, \bar{l}_2, \bar{l}_3),\ \bar{l}_i = -l_i;\\
&i = 1, 2, 3;
\end{aligned} \tag{2}$$

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(1) (a) "Lattice Energy of $PbSO_4$, $BaSO_4$, $SrSO_4$ and $CaSO_4$." Unpublished thesis, Hirosima Univ., 1942; revised and enlarged, 1946—51, ("Physical Chemistry of a Radical Ion $SO_4{}^{--}$,") Jan. 1951—; (b) "Lattice Energy…… I. Electrostatic Potential Energy." Oral report, *Nippon-Buturi-Gakkai.Si* **4**, 64 (1949).

(2) *This intention was suggested to me in 1942* by the late Prof. Yōzo Kobayashi (1895—1945).

(3) In regard to ionic crystals with radical ions several reports have been issued since 1926 on the (electrostatic) lattice energy whose values were obtained by means of computing lattice sums; these radical ions are: $CO_3{}^{--}$, $NO_3{}^-$, $BO_3{}^{---}$, $HF_2{}^-$, $N_3{}^-$, $BF_4{}^-$, $NH_4{}^+$, CN^-, OH^-, SH^-, SeH^-, $C_2{}^{--}$, $O_2{}^-$, and $O_3{}^-$. On the other hand, Kapustinskiĭ (1933, 1943) offered a general expression that gives, without performance of lattice summations, a rough value of the lattice energy, and for radical ions it has been utilized since 1935 by several Soviet investigators; above all, extensively by Yatsimirskiĭ since 1947.

(4) B. Y. Oke: (a) *Proc. Indian Acad. Sci.*, **4A**, 1 (1936); (b) ibid., **5A**, 326 (1937).

(5) T. Matsuhara [-bara] and T. Nagamiya, *Sci. Papers Osaka Univ.*, No. 14, pp. 17 (1949).

(6) As for a crystal with the structure of small degree of symmetry the constancy of the so-called Madelung's constant is not perfect; accordingly, it might be proper to adopt the term "coefficient" (or "factor") in general as a substitute for the term "constant."

(7) Cf.: M. Born, "Atomtheorie des festen Zustandes," 1923, from which are taken several symbols used here: δ, a_l, s, $\vec{r}^{\,l}_{kk'}$ etc., l_i etc., S, Σ, S' etc., $\vec{q}^{\,l}$, — on Y, ε, and $G(x)$. Notice: C. N. Wall, *Phys. Rev.*, **36**, 1243 (1930); R. H. Canfield, ibid., **40**, 1034 (1932); W. J. Taylor, *idid.*, **77**, 763 (1950); G. Molière, *Z. Krist.*, **101**, 383 (1939).

(8) P. P. Ewald, *Ann. Physik*, [4] **64**, 253 (1921).

where h ("intramolecular index") and ν correspond to k and s, resp., σ is the number of the "molecules" in a cell, z_h the valency of an ion as particle h, and S with $\bar{l}$ and $\sum$ with (kk') denote such a summation that a pair of indices l & $\bar{l}$ and a pair of permutations of indices kk' & $k'k$, resp., be counted once only.

In the case of a z-z-valent compound it is suitable for comparison to introduce a derived quantity M_a/z^2. The linear size, χ, of a molecule may be defined by

$$\chi=(V/N)^{1/3}=\delta/\sigma^{1/3} \qquad (3)$$

where V is the molal volume; and the adoption of $M\chi$ as M_a is also valuable in some cases.

2.2) The rectangular crystal lattice.—The preceding set of expressions of M_a may be specified so as to fit to the rectangular crystal lattice in the following form:

$$\begin{aligned}
&\delta^3=\prod_i a_i;\ \ L=\frac{1}{2}\underset{\mathring{l}}{\mathrm{S}'}c_l L_l+(2/s)\underset{\bar{l}}{\mathrm{S}'}X_l L_l,\\
&\lambda_l=(d/a_1)^2\sum_i(a_1/a_i)^2 l_i^2,\\
&X_1=(\nu/\sum_h z_h^2)\sum_{(kk')}{}' z_k z_{k'}\cos 2\pi\sum_i(k_i-k_i')l_i;\\
&\bar{Y}=\frac{1}{2}\underset{\mathring{l}}{\mathrm{S}'}c_l\bar{Y},\quad \bar{\eta}=(a_1/d)\{\sum_i(a_i/a_1)^2 l_i^2\}^{\frac{1}{2}};\\
&\overset{l}{\eta}{}_{kk'}=(a_1/d)\{\sum_i(a_i/a_1)^2(k_i-k_i'+l_i)^2\}^{\frac{1}{2}};\\
&\mathring{l}=(\mathring{l}_1,\ \mathring{l}_2,\ \mathring{l}_3),\ \mathring{l}_i=|\,l_i\,|\,;\\
&c_l=2^\mu,\ \mu=0,\ 1,\ 2,\ 3; \qquad (4)
\end{aligned}$$

where S with $\mathring{l}$ denotes such a summation that a set of like cells with one and the same value of $\mathring{l}$ be counted once only, c_l is the number of these like cells in a set, and μ the number of the nonzero components of $\mathring{l}$.

In case that X_l depends solely on the absolute values (regardless of the signs) of the components of l, i. e.,

$$X_l=X_l(\mathring{l}) \qquad (5)$$

further simplification may be brought about, thus

$$L=\frac{1}{2}\underset{\mathring{l}}{\mathrm{S}'}c_l w_l L_l \qquad (6)$$

In § 3.2 and 4 the numerical calculation of $M_\delta(=Ma_1\delta/a_1)$ is made in the two selected cases:

$$(1)\quad \varepsilon=\varepsilon^0=\pi/d \qquad (2)\quad \varepsilon=\varepsilon'=\pi/d\sqrt{2}$$

$$\text{with } d=a_1 \text{ (but finally } d=\delta) \qquad (7)$$

§ 3. Verification of the Expressions of M_δ

3.1) The cubic case NaCl.(9a)—After the expressions of M_δ for the cubic crystal lattice had been derived from those given in § 2, they were applied to the case of NaCl, the numerical calculations with the three selected values of ε producing for M_δ the values $3.49512918926\underline{6}_{48\pm17}$, $\cdots\underline{6}3_{24\pm48}$, and $\cdots\underline{6}3643_{25\pm17}$ molec^{-1}. cell$^{-1/3}$. These values coincide not only with each other perfectly but also with Emersleben's corresponding one practically. This fact seems to support the reliability of all the above-mentioned expressions for M_a or M_δ and of the mode of handling them.

3.2) The rhombic case $CaCO_3$.(9b)—The expressions of M_δ given in § 2 were applied to the rhombic case of $CaCO_3$, and the numerical calculations (cf. Eq. 7), being carried out by use of the same data for the crystal structure as used by Oke(4) but in a fashion somewhat different from his, produced for M_δ the values $12.8472\underline{3}_9$ and $\cdots\underline{3}_3$ molec^{-1}. cell$^{-1/3}$. The fact that they perfectly coincide will be satisfactory. While, on the other hand, the agreement between each of them and Oke's corresponding one is not satisfactory, since there is a discrepancy of 11% between them. This poor agreement, however, was found(9c) to be caused by the inaccurateness in the value of Oke.

§ 4. Calculation(10) of Madelung's Coefficient M_δ

With the two applications in § 3 as preliminary, the set of expressions of M_δ is now applied to the crystals of the four sulfates in which the author has become interested. These four cases shown in the title are designated by a′, a″, a‴, and b, resp.

4.1) Data for the crystal structure(11)(12)—

State: 0—30° C, 1 atm. Rhombic; a: $BaSO_4$ type, b: $CaSO_4$ type; $\sigma=4$ molec. cell^{-1}; $\nu=2$ part. molec^{-1}—$Me^{++}+SO_4^{--}$(13) (8)

In Case a, an approximate fraction is selected for the value of each parameter, and the adopted values are:(14)

$$v\approx\frac{24}{72},\ u\approx\frac{23}{72},\ v'\approx\frac{50}{72},\ u'\approx\frac{68}{72} \qquad (9a)$$

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(9) For details, see the three papers (a, b, and c) in *J. Sci. Hiroshima Univ.*, Ser. A, **16**, No. 3 (1953), where (a) Emersleben's and (c) Oke's works are touched upon with comment.

(10) For details, see *J. Sci. Hiroshima Univ*, Ser. A, **16**, No. 3 (1953).

(11) Mainly, R. W. G. Wyckoff: (a) "The Structure of Crystals," 2. ed., 1931—see also (b) "Crystal Structures," Vol. II, 1951.

(12) The values of $a:b:c$ are taken from: "J. D. Dana: The System of Mineralogy," 6th ed., 1915. For its 7th ed., Vol. II, 1951, see Note 4b of Ref. 10.

(13) Here, the electricity is assumed to be located at the center of SO_4^{--} (i. e., of its S) as well as of Me^{++} as a point charge.

(14) The magnitudes of the error thereby caused are: −42, 36, −3, 14; −55, 14, −3 124; and −55, −14, −3, 14 (resp.) $\times 10^{-4}$. If we adopt $u'\gtrsim 67/72$ instead, each last number becomes −124, −14, or −124, resp.

Table 1

i			1, +2		2, −2
ii	1	2	3	4	5—8
iiia	$\frac{1}{4}, v, u$	$\frac{3}{4}, \bar{v}, \bar{u}$	$\frac{1}{4}, \frac{1}{2}-v, \frac{1}{2}+u$	$\frac{3}{4}, \frac{1}{2}+v, \frac{1}{2}-u$	(v', u')
iiib	$u, \frac{1}{4}, 0$	$\bar{u}, \frac{3}{4}, 0$	$\frac{1}{2}+u, \frac{1}{4}, \frac{1}{2}$	$\frac{1}{2}-u, \frac{3}{4}, \frac{1}{2}$	(u')

Case	a′		a′′		a′′′		b	
iv	1:1.28939:1.57032		1:1.31359:1.63040		1:1.28005:1.55790		0.89325:1:1.0008	
v	0.33_{75} 0.31_{58}	0.69_{47} 0.94_{30}	0.33_{88} 0.31_{80}	0.69_{47} 0.93_{20}	0.33_{88} 0.32_{08}	0.69_{47} 0.94_{30}	0.65	0.15

i: h, z_h. ii: k. iii: Atomic positions. iv: $a_1:a_2:a_3$ (a:) $=b^*:c^*:a^*=b:c:2a$ or (b:) $=a^*:b^*:c^*=a:b:c$, where a^*, b^*, c^* are the (röntgenoscopical) lattice constants and $a:b:c$ is the (morphometrical) axial ratio. v: Parameters (a:) $\frac{vv'}{uu'}$ or (b:) uu'.

In Case b, without artificial approximation,

$$u=\frac{13}{20}, \quad u'=\frac{3}{20} \tag{9b}$$

4.2) Calculated values of M_δ (to be amended in § 6).—Each couple (cf. Eq. 7) of numerical values for M_δ obtained by calculation is given in Table 2. The coincidence between them seems so perfect that they conform to the verification of accounts in Ewald's method. Every one of these four values might be acceptable, from the standpoint assumed in the author's other paper,(15) as of reasonable magnitude.

Table 2

M_δ	$PbSO_4$	$BaSO_4$	$SrSO_4$	$CaSO_4$
Case 1	13.16377_3	13.18779_4	13.15651_2	13.50363_5
〃 2	$\ldots 75_8$	$\ldots 78_5$	$\ldots 51_0$	$\ldots 62_7$

§ 5. Estimation of the Uncertainty in the Calculated Value of M_δ

5.1) General remark.—The error with which the value of M_δ calculated in this mode is expected to be accompanied may be analyzed—as mentioned in Ref. 9b, § 2.3—into three sorts of errors, which are to be discussed in some detail.

5.2) The error from computation.—The main error (i) of computation comes from that reduction of the decimal to its approximate fraction which is done in Eq. 9a concerning the parameters of atomic positions. A rough value for it has been merely indirectly estimated to be 0.2%.(16) On the other hand, the ordinary computational error (ii) must be only subordinate, because the two calculated values for M_δ coincide to the extent of 10^{-4}%.

5.3) The error from theory.—Several assumptions underlying the method of this calculation are to be mentioned here. The matters concerning the grain size, the imperfection of a crystal (such as the mosaic structure and the lattice defect), and the thermal motion of the constituent particles may be insignificant in ordinary cases; the question of chemical purity of the material will rather be regarded as a matter of experiment.

On the other hand, several difficulties are encountered when we consider the following aspects peculiar to our subject. The character of the bonds between ions in these crystals is—though mainly ionic—in a fair measure, covalent owing to the small degree of symmetry in the crystal structure and of uniformity in the ionic distribution, not a little polarizability of the radical (sulfate) ion in particular, the bivalency of the ions, and the great polarizing influence by lead ion and that by calcium ion. Yet, this crystal system retains rectangular symmetry, the distribution of the neighboring anions around a cation (or the reverse) is passably uniform and the coordination number(17) of an ion is no less than some value between 5 and 7, the deformability of sulfate ion is by no means great,(18) and the shape of sulfate ion is of regular tetrahedron, though slightly distorted. Consequently, the assumption(13) made about the distribution of electric charges, i. e., the purely ionic bonding between point charges (with certain integral multiples of the electric elementary quantum) at the assigned sites, will be practically not far from reality. Furthermore, it is to be noticed that the electrostatic potential energy of a crystal lattice may be regarded as a quantity *defined*, in a

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(15) Ref. 9c, Art. V.

(16) In Case b, which is free from this error and in which the crystal structure bears a close resemblance to that in Case a, another calculation has been executed with the values $u-\frac{1}{2}=u'=0.1$ (besides, 0, 0.05, 0.2, and 0.25), producing for M_δ the numerical value 12.9941_1. Certain considerations have then been made with such materials as Eq. 9b, Note 14, and Table 7 of Ref. 10 (including the sub-table for $CaSO_4$ with $u'=0.1$) and with a certain possible supplementary assumption.

(17) In these crystals we cannot definitely assign to this quantity any discrete number. Cf. Table 6 of Ref. 10, where η_p is proportional to the interionic distance and (a) the five or (b) the three $-\frac{1}{4}d_{kk'}{}'_{p}$'s are, so to speak, the "components" of the coordination number.

(18) "[Geiger-Scheel.] Handbuch der Physik," Bd. XXIV/2 (2. Aufl.), 1933, Kap. 6 (by H. G. Grimm and H. Wolff), Ziffn. 61, 64—66, esp. Tab. 62.

certain sense (so far as the present state of our knowledge is concerned), on the basis of an assumption such as mentioned above, the possibility(19) of the subsequent step to approximation being left to a later estimation of the whole potential energy (or, further, the total energy in the thermodynamic signification).

The magnitude of the error originating from theory is, accordingly, somewhat indefinite, and so it is difficult to be estimated; still the author will give it a value 0.5%, if necessary.

5.4) The error from experiment.—M_δ depends upon the axial ratio ($a{:}b{:}c$) and the parameters of atomic positions (briefly, parameters). These quantities vary with temperature and pressure and, from a practical viewpoint, with chemical purity (and certain physical matters mentioned in Art. 3). The error due to these variations and that due to measurement constitute together the total experimental error.

In regard to variation in the magnitudes of the parameters we have as yet no information, while the magnitudes of the variabilities of $a{:}b{:}c$ are known for some of these crystals and are shown in Table 3.(20)~(23) It will be seen from this table that any datum with such specification as "at some ordinary temperature and pressure" suffices for our present purpose and, at the same time, that the experimental error in $a{:}b{:}c$ of No. 1 is less than 0.3%. The effect of uncertainty in $a{:}b{:}c$ upon M_δ is not simple in nature and might scarcely be estimated exactly unless we execute several sets of calculations. Nevertheless, the author will try to form a very rough estimate of it.

Table 3

No.	a′	b
1	0.78516:1:1.28939	0.89325:1:1.0008
2	0.7852 (−62°) 1.2891	0.8911 (−64°) 0.9996
3	0.7894 (514°) 1.2870	0.8996 (500°) 1.0025
4	7.3 −3.6	15.1 5.5
	a″	**a‴**
1	0.81520:1:1.31359	0.77895:1:1.28005
2	0.8161 (−60°) 1.3121	0.7785 (−62°) 1.2821
3	0.8124 (570°) 7.3047	0.7794 (550°) 1.2780
4	−5.9 −11.7	1.5 −6.7
5	1.431 2.252 1.490†	1.920 1.851 1.490
6	−6.7 −10.0	0.54 −6.4
7	5.221 6.757 5.194	6.222 4.406 4.462
8	1.25 2.05	−1.41 −0.072
9	0.81^{6}_{2} :1:1.31$^{5}_{0}$	0.7$^{9717}_{6964}$:1:1.$^{30010}_{25506}$
10	0.8146 :1:1.3119	0.78093:1:1.28324††
11	0.81439:1:1.31223	——

1: Axial ratio (a. r.) adopted in Table 1. 2, 3: A. r. at the temp. indicated. 4, 6: Mean increments per deg. in a. r., in 10^{-6} deg.$^{-1}$. 5: Coeffs. of linear thermal expansion at 0—100° C, in 10^{-5} deg^{-1}. 7: Linear compressibilities at 23—26° C, 0 atm., in 10^{-7} bar^{-1}. 8: Increments per bar in a. r., in 10^{-7} bar^{-1}. 9: A. r. of various minerals. 10: A. r. of a pure mineral. 11: A. r. from a^*, b^*, c^* adopted by Wyckoff. † For the new data, see S. S. Sharma, *Proc. Indian Acad. Sci.*, **33A**, 283 (1951). †† See also Note 4b of Ref. 10.

Now the three crystals of the barite type have been considered, in Eq. 9a, to have the same value for each parameter, and so the distinction between these crystals will remain solely in $a{:}b{:}c$. These calculations may, therefore, be regarded as having been made on such a crystal of one and the same compound as with three different experimental values for $a{:}b{:}c$. There is then constructed a table (Table 4a) that shows the relation between M_δ and $a{:}b{:}c$. It is seen from this table that, for this special case (in which a/b and c/b alter alike in both magnitude and sign), the quotient $2M_\delta/\{(b/a)\varDelta(a/b)+(b/c)\varDelta(c/b)\}$ is at most *ca.* 0.07.(24)

Table 4a

No.	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
$BaSO_4$	···				···			
B−P		300, 242	376, 186	281		240	18.2	0.065
$PbSO_4$	···				···			
P−S		62, 93	80, 73	76		73	5.5	0.072
$SrSO_4$	···				···			

1: A. r. in Table 3, No. 1. 2: Differences in a. r. between the crystals, as indicated by B−P or P−S. 3: Quotients (2)÷(1). 4: Arithmetical mean of the quotients in (3). 5: M_δ in Table 2. 6: Difference in M_δ similar to (2). 7: Quotient (6)÷(5). 8: Quotient (7)÷(4). In Nos. 2-4, 6, and 7 the unit is 10^{-4}.

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(19) E. g., the mode of treatment in Ref. 5.

(20) Nos. 2, 3. R. Kolb's, through *Chem. Zentr.*, **1911**, I, 1317.

(21) Nos. 5, 9, 10. "Gmelins Handbuch," 8. Aufl. The values for a^*, b^*, c^* recommended in this book give 0.81342 : 1 : 1.31066.

(22) No. 7. Values calculated by the present author from: P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **77**, 187 (1949).

(23) No. 11. Ref. 11b. In this book Walton and Walden's work is cited; their values for a^*, b^*, c^* of a pure artificial crystal at 24—30°C give 0.81326 : 1 : 1.31124.

(24) In a preliminary calculation (Case α) I adopted for $a:b:c$ the values derived from those of the lattice constants quoted in Ref. 11a. The values (Case α) that correspond to those (Case β) in Table 4a are: No. 1—0.816630 : 1 : 1.316079, 0.785316 : 1 : 1.288104, 0.779851 : 1 : 1.276119; No. 5—13.1883_6, 13.1637_7, 13.1572_6 : No. 8—0.063, 0.061; and for $CaSO_4$ No. 1—0.893525 : 1 : 1.001439; No. 5—13.50251. If we construct a table which is similar to Table 4a and in which a combination $\beta\alpha$ is taken for each crystal, the values corresponding to those in Table 4a, No. 8, in the order of B, P, S, and C, are: 0.049, -0.00_0, −0.059, and −0.175. If such a weighted mean as $\{10(b/a)\varDelta(a/b)+(b/c)\varDelta(c/b)\}/11$ is taken instead of the arithmetical mean in No. 4, the above-mentioned eight values for No. 8 become; 51, 70; 51, 69; 50, 02±20, 74, and −246 (resp.) $\times 10^{-3}$. After such complementary considerations it will be found admissible to adopt the magnitude *ca.* 0.07 for Case a or *ca.* −0.2 for Case b.

After all, the error (i) in M_δ due to uncertainty in $a:b:c$ will not exceed $(0.3\% \times 0.07 \approx)$ 0.02% in Case a, while in Case b,(24) possibly, 0.05%. On the other hand, the error (ii) due to uncertainty in the parameters does not, presumably, differ much from the amount 0.2% mentioned in Art. 2 in Case a, and in Case b this error is estimated(25) to be *ca.* 0.4%.

§ 6. Values of M_δ with Their Probable Errors

The purity of the materials whose values of the axial ratio are adopted in these calculations (§ 4) is unknown to the present author. With respect to $BaSO_4$ and $SrSO_4$, however, certain reported values are for chemically pure crystals or are designated as recommended ones.(26) They are now adopted and the values of M_δ in Table 2 are amended by utilizing the consideration made in § 5.4. In Table 5 each final value of M_δ is given, to which both its probable error, estimated(27) in § 5, and its corresponding axial ratio are appended. The corresponding values of $M\chi/z^2$ are: 2.0_{73}, 2.0_{77}, 2.0_{72}, and 2.1_{27} (resp.) $\text{molec}^{-4/3}$.-valency^{-2}.

Table 5

Madelung's Coefficients (M_δ) of the Sulfates at 0—30°C

(δ: Mean lattice constant. Unit: $\text{molec}^{-1}.\text{cell}^{-1/3}$)

	$PbSO_4$	$BaSO_4$
M_δ	13.164±0.7%	13.187±0.7%
$a:b:c$	$0.78_{52}:1:1.28_{94}$	0.814:1:1.312
	$SrSO_4$	$CaSO_4$
M_δ	13.159±0.7%	13.504±0.9%
$a:b:c$	$0.78_{69}:1:1.28_{32}$	$0.89_{32}:1:1.00_{08}$

§ 7. Rates of Variation in M_δ with Temperature and Pressure

By utilizing the consideration made in § 5.4 a rough estimation of the variability of (viz. the rate of variation in) M_δ with temperature or pressure has been made,(25) producing the results: $-(\partial M_\delta/\partial T)_P{}^*/M_\delta$, in $10^{-7}\,\text{deg}^{-1}$: 5, -4 or -4,(29) 0.9 or 0.1, and -20; $(\partial M_\delta/\partial P)_T{}^*/M_\delta$, in 10^{-9}-bar^{-1}: —, 8, -7, and —; for Cases a′, ...b, resp.; where * means that the parameters of atomic positions are assumed to be kept constant. Thence it is seen that the (absolute) magnitudes of these two quantities are 10^{-2} of those of the mean linear thermal expansibility and of the mean linear compressibility, respectively.

§ 8. Values of the Electrostatic Lattice Energy Φ_1

The molal electrostatic potential energy, Φ_1, of a crystal lattice may be computed by use of Eq. 1 with $d=\delta$; while (cf. Eqs. 3, 4)

$$\delta^3 = a_1 a_2 a_3 = \sigma V/N = \sigma M/\rho N \tag{10}$$

where M is the gram-formula mass and ρ the density. The values of Φ_1 thus computed(30) are shown in Table 6.(31) Every one of them is accurate to *ca.* 1%, but the relative error, viz. the error in each difference between them, may probably be much less than (possibly, *ca.* 1/6 of) the corresponding sum of their independent errors. (This statement is valid also for M_δ in § 6.)

Table 6

Electrostatic Lattice Energies (Φ_1) of the Sulfates, with their corresponding quantities of ρ and δ, at 25° C

	$PbSO_4$	$BaSO_4$
i ρ	6.37±0.02	4.49±0.01
ii δ	6.812±0.007	7.015±0.005
iii $-\Phi_1$	641.6±5.1	624.1±4.8
	$SrSO_4$	$CaSO_4$
i ρ	3.97±0.01	2.98±0.02
ii δ	6.748±0.006	6.719±0.015
iii $-\Phi_1$	647.5±5.1	667.3±7.5

Unit. i: g.cm^{-3} ii: $\text{Å.cell}^{-1/3}$
iii: kcal.mol^{-1}

The rate of variation in Φ_1 with temperature or pressure will be approximately equal to the minus mean linear thermal expansibility or the mean linear compressibility, resp., if we refer to § 7 and assume that the corresponding rate of variation in M_δ due to the parameters of atomic positions may be small enough.

Summary

A plan for investigation of the physical chemistry of radical ions is stated with especial reference to the strict treatment of the lattice-energy problem and the treatment of complex ionic crystals. First, the expressions suitable for the practical numerical calculation of

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(25) The experimental error in u or $u\prime$ being supposed to be 0.005, an interpolation is made between the values 13.50 and 12.99—refer to Note 16 and Tables 1 (v) and 2.

(26) Cf. Table 3 (Nos. 10, 11) and Notes 21, 23.

(27) In Case a the errors 2-i and 4-ii are counted once collectively.

(28) The materials in Tables 3 (Nos. 2—8) and 4a (No. 8) and in Note 24 have been used.

(29) A set of the data in Ref. † of Table 3 leads to -5 for both 25° and 0—100° C.

(30) The values adopted are: M's, and N, e, and cal in *J. Am. Chem. Soc.*, **74**, 2447, 2699 (1952); σ in Eq. 8; and ρ's selected from various sources, esp. from Liter. 4b of Ref. 10.

(31) The corresponding values of the lattice constants a^*, b^*, c^*, in $\text{kx.cell}^{-1/3}$, computed by use of the values of $a:b:c$ in Table 5 and of λ_g/λ_s ($1.00202\ \text{kx.Å}^{-1}$), are: 8.439, 5.374, 6.929; 8.850, 5.436, 7.132; 8·342, 5.341, 6.854; and 6.218, 6.961, 6.967; resp.

Madelung's coefficient of the general and the rectangular crystal lattice are derived from Ewald's original general expressions. Next, they are verified in the two simple cases, NaCl and the rhombic $CaCO_3$, by means of numerical application. Then, they are applied to the more complex cases, i. e., the rhombic crystals of $PbSO_4$, $BaSO_4$, $SrSO_4$, and $CaSO_4$, with SO_4^{--} which is assumed to be a point charge. The degree of accuracy of the calculated values is further discussed; and, in connection with it, an attempt is made to estimate the extent of variability of Madelung's "coefficient" (or "constant," as it is called). Finally, the electrostatic lattice energy is evaluated.

I express my sincere thanks to the late Dr. Y. Kobayashi, who introduced me to this problem. I am grateful to Professor Tamamushi for his encouragement and kindness in reading my original manuscript. I am also indebted to Assist. Prof. M. Miura, who has afforded facilities for continuing my work, and to Assist. Prof. E. Hirahara for his valuable advice.

Department of Chemistry, Hirosima University of Literature and Science, Hirosima