	$-\Delta\mu_h$ (calcd.)(a)	$-\Delta\mu_h$ (calcd.)(b)	$-\Delta\mu_h$ (exptl.)
Li$^+$	114	154	125.6
Be^{+2}	554	779	591

Fluoride ion presents a special problem. The value for the free energy of hydration tabulated by Noyes appears to be consistent with the present model (Table III). This value, however, was calculated from the data for gaseous fluoride ion in the National Bureau of Standards Circular 500; more recent work[12] shows fairly conclusively that this entry is wrong. Revision leads to a free energy of hydration (on the present scale) of -98 kcal. mole^{-1} for fluoride ion. This cannot be accounted for on the present model, since it is numerically greater than the self energy of the ion *in vacuo*. The discrepancy is made worse if we assume, as is probable for this anion on the evidence of its mobility and dielectric constant depression, a layer of partially immobilized water molecules around it. This would increase its self energy from the value of 1.6 kcal. shown in Table III to about 10 kcal. mole^{-1}, making the calculated hydration energy about -73 kcal. mole^{-1}. Thus the free energy of aqueous fluoride ion appears to be between 17 and 25 kcal. mole^{-1} lower than can be explained on the electrostatic model. A reasonable explanation of this could lie in the formation of several "hydrogen bonds" between the fluoride ion and the water molecules surrounding it. In other terms, the "proton affinity" of fluoride ion is high compared with the other halide ions.

The striking success of the model in accounting for the hydration energies of cations, including multiply charged ones, justifies the claim that the present method of calculating self energies of gaseous ions is a marked advance on the use of the crystal radii.

Some Comments on the Model.—The transfer of the ion from the gas state to solution is envisaged as being carried out directly rather than through a discharge–transfer–recharge process, since the latter is difficult to visualize for actual ions which can be "neutralized" only by conversion to atoms, and raises some difficult problems about the solvation of electrons. The direct transfer really involves the question of the energy for

(12) J. E. B. Randles, *Trans. Faraday Soc.*, **52**, 1573 (1956).

moving the ion through the interfacial potential at the water surface, as discussed by Randles.[12] This term is zeV where V is the interfacial potential, a constant at constant temperature even though its actual value is still in doubt. A term with the necessary dependence on the charge of the ion has been introduced *via* the quantity $z\Delta F°_H$ of eq. 9, which may be taken to include the interfacial potential term. This term appears only when separate ionic values are discussed, and may be thought of as a penalty for using quantities not determinable by direct experiment. It vanishes when we consider either energies of electrically equivalent numbers of cations and anions together, or energy differences between equivalent amounts of ions of the same sign.

While the model proposed gives a very satisfactory account of the free energy of hydration, it cannot be expected to deal adequately with the entropy. The entropy of the gaseous ion does not involve an electrostatic term and is fully calculable from the Sackur–Tetrode equation; but that of the aqueous ion will involve the change with temperature of several of the quantities in eq. 4. Only that of ϵ is known, and its contribution is probably the least important. One could of course estimate the changes in n or r_w with temperature needed to produce agreement, but this would not constitute an explanation of the entropy of hydration. For this more sensitive test, detailed consideration of the modes of motion of water molecules near the ion would be required in addition to the relatively crude electrostatic approximation for more remote molecules. Dr. L. G. Hepler is currently working on this problem and on that of the free energy of transfer of ions between different solvents.

The reduction in size of the ion on solution in water would appear to require a compression energy which has been disregarded in this paper. This question is discussed for the closely related case of the formation of an ionic crystal from gaseous ions in the following paper, and the answer suggested in that case is probably relevant, *mutatis mutandis*, to the present situation. In brief, the ions are not compressed; rather, as a necessary consequence of the virial theorem, they shrink in the wash.

Crystal Lattice Energies and the Electrostatic Self Energies of Gaseous Ions

BY R. H. STOKES

The self energies of gaseous ions, calculated from their van der Waals radii by the method of a previous paper, show a striking correlation with crystal lattice energies. For ions of the noble gas electronic structure, the lattice energy of a crystal in which the cations and anions have equal van der Waals radii is simply the negative of the self energy of the gaseous ions. For ions of unequal size, the difference between these two energies is a linear function of the radius ratio of the gaseous ions; a single slope characterizes large groups of crystals. A tentative explanation of these observations is suggested in terms of a simple electrostatic model taking account of the deformation of the ions in the crystal.

Introduction

The writer has recently shown[1] that it is possible to calculate the van der Waals radii of gaseous ions of the

(1) R. H. Stokes, *J. Am. Chem. Soc.*, **86**, 979 (1964).

noble gas structure from data on the noble gases themselves. Consideration of the electrostatic self energies of the gaseous ions calculated by treating the ion as a sphere of charge ze having the van der Waals radius r^v

led to a very satisfactory quantitative account of the hydration energies of cations of charge $+1$, $+2$, and $+3$, using a physically reasonable model for the aqueous ion.

It seemed likely that a similar approach to the lattice energy of crystals would be of value. The present paper describes some results which are of especial interest in that the lattice energy is found to be a simple function of the gaseous ion radii. Only one fixed parameter is needed to give the lattice energies of a large class of crystals, without appeal to experimental data on the crystal structure or dimensions.

Experimental Lattice Energies.—The lattice energy E_L is defined as the energy change in the process

gaseous ions at infinite separation $\longrightarrow$ crystal, $\Delta H = E_L$ (1)

In some cases[2] it has been possible to determine this energy change fairly directly by combining measurements of the heat of vaporization of the crystal into gaseous "molecules" (or ion pairs) with data for the dissociation energy of the "molecule" in the gas into free ions. More often, however, the lattice energy is obtained, in the case of halide salts, from a combination of data for: (a) the heat of formation of the crystal from its elements, (b) the vaporization of the metal to gaseous atoms, (c) the (spectroscopic) ionization potential of the metal, (d) the heat of dissociation of the halogen to gaseous atoms, (e) the electron affinity of the halogen atom.

The greatest uncertainty in the calculation is usually that for process (e), though a large revision of the value for process (d) has been made for fluorine in the last decade or so. The electron affinities of the halogens are in fact often estimated from calculated crystal energies, but values so obtained are naturally subject to the assumption that the Madelung–Born–Mayer treatment of the lattice energy is final and definitive. Cubicciotti[3] has summarized the direct experimental determinations of the electron affinity, the methods used being: space charge, magnetron, electron impact, and surface ionization. Weighting these various measurements according to the estimated uncertainties which he tabulates, the following values are obtained, with uncertainties of ~ 2 kcal. mole^{-1}.

$$X(atom, g) \longrightarrow X^-(g), \Delta H_e(X) \quad (2)$$
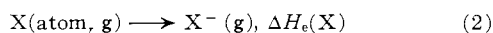
$\Delta H_e(F) = -82.5$ kcal. mole^{-1}
$\Delta H_e(Cl) = -86.2$ kcal. mole^{-1}
$\Delta H_e(Br) = -81.7$ kcal. mole^{-1}
$\Delta H_e(I) = -73.6$ kcal. mole^{-1}

These values have been combined with those for the processes (a), (b + c), and (d) above given in N.B.S.[4] Circular 500, except that for the process

$$F_2(g) \longrightarrow 2F(g)$$
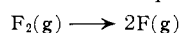
the value $\Delta H°_{298} = +37.5$ kcal. mole^{-1} has been adopted.[5] Strictly speaking, of course, the lattice energy refers to process 1 carried out at $0°K.$, but the corrections are small, involving the zero-point energy of the crystal and the difference between the heat ca-

(2) L. Helmholz and J. E. Mayer, *J. Chem. Phys.*, **2**, 245 (1934); also L. Brewer and E. Brackett, *Chem. Rev.*, **61**, 425 (1961).

(3) D. Cubicciotti, *J. Chem. Phys.*, **31**, 1646 (1959). Since the compilation of Cubicciotti's data, direct spectroscopic measurements of the energy required to liberate an electron from gaseous halide ions have been reported by R. S. Berry and C. W. Reimann (*ibid.*, **38**, 1540 (1963)). The gaseous ions were produced in shock-heated vapors in sufficient quantity to make direct measurement of the absorption spectrum of the ion possible. Their values for $\Delta H_e(X)$/kcal. in process 2 are F, -79.5; Cl, -83.3; Br, -77.5; I, -70.6, with estimated uncertainties less than 0.1 kcal. The use of these data would alter the experimental lattice energies in Table 1 by 2–4 kcal. per mole of halide ion, but would not seriously affect the conclusions.

(4) F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Govt. Printing Office, Washington, D. C., 1952.

(5) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

TABLE I

RELATION BETWEEN LATTICE ENERGY AND SELF ENERGY OF GASEOUS IONS[a]

(a)	(b)	(c)	(d)	(e)	(f)
			$r_1{}^v/r_1{}^v$	$-E_L$	
Salt	$-E_L$(exptl.)	$\Sigma E_s{}^v$(gas)	(gas)	(calcd., eq. 7)	δ, %
LiF	245.6	232.7	1.676	...	...
LiCl	203.4	219.4	1.977	204.5	+0.5
LiBr	191.6	217.9	2.018	192.6	+ .5
LiI	179.6	210.8	2.237	180.0	+ .2
NaF	218.4	209.8	1.412	...	...
NaCl	187.0	196.5	1.664	186.4	−0.3
NaBr	177.2	195.0	1.700	177.6	+ .2
NaI	166.7	187.9	1.887	165.8	− .5
KF	194.0	186.3	1.142	...	...
KCl	170.1	173.0	1.346	167.7	−1.4
KBr	161.8	171.5	1.374	162.2	+0.3
KI	153.3	164.4	1.525	151.3	−1.3
RbF	184.1	179.2	1.060	...	...
RbCl	162.1	165.9	1.247	162.1	0.0
RbBr	154.4	164.4	1.274	157.6	+2.1
RbI	146.8	157.3	1.413	147.0	+0.1
CsF	173.4	170.1	0.955	...	...
CsCl	156.4	156.8	1.126	154.9	−1.0
CsBr	149.4	155.3	1.150	151.6	+1.5
CsI	142.5	148.2	1.277	141.3	−0.8

Mean δ $\pm 0.7\%$

Chlorides, $\alpha = 0.092$ Å.$^{-1}$; bromides and iodides, $\alpha = 0.150$ Å.$^{-1}$

BeF$_2$	839	973	2.297	...	...
BeCl$_2$	720	946	2.710	719	−0.1
BeBr$_2$	692	943	2.765	709	+2.5
BeI$_2$	665	929	3.066	655	−1.5
MgF$_2$	700	737	1.618	...	...
MgCl$_2$	599	710	1.908	590	−1.4
MgBr$_2$	575	707	1.947	581	+1.0
MgI$_2$	547	693	2.159	539	−1.5
CaF$_2$	628	623	1.290	...	...
CaCl$_2$	537	596	1.522	527	−1.9
CaBr$_2$	514	593	1.553	520	+1.2
CaI$_2$	491	579	1.722	483	+1.6
SrF$_2$	592	583	1.175	...	...
SrCl$_2$	509	556	1.386	505	−0.8
SrBr$_2$	488	553	1.414	498	+2.0
SrI$_2$	463	539	1.568	464	+0.2
BaF$_2$	557	543	1.059	...	...
BaCl$_2$	485	516	1.250	483	−0.4
BaBr$_2$	466	513	1.275	476	+2.2
BaI$_2$	439	499	1.414	444	+1.2
AlF$_3$	1415	1689	1.825	...	...
AlCl$_3$	1289	1649	2.155	1304	+1.1
AlBr$_3$	1267	1645	2.196	1287	+1.0
AlI$_3$	1232	1623	2.435	1194	−2.9
ScCl$_3$	1163	1346	1.692	1139	−2.1
ScBr$_3$	1130	1342	1.730	1124	−0.5
YCl$_3$	1076	1230	1.518	1075	−0.1
YI$_3$	1009	1204	1.720	989	−2.0
LaCl$_3$	1016	1131	1.370	1020	+0.4
LaI$_3$	944	1105	1.551	940	−0.4

Mean δ $\pm 1.25\%$

For all these chlorides, bromides, and iodides, $\alpha = 0.200$ Å.$^{-1}$

[a] All energies in kcal. mole^{-1}; $\Sigma E_s{}^v$ calculated from gaseous ion van der Waals radii of reference 1; 1 = cation, 2 = anion.

pacities of the crystal and the gaseous ions. Examination of Table VI of reference 3 shows that the errors introduced by identifying the lattice energy at $298°K.$ with that at $0°K.$ seldom exceed 1 kcal. mole^{-1}; this is less than the uncertainty in the electron affinities. The
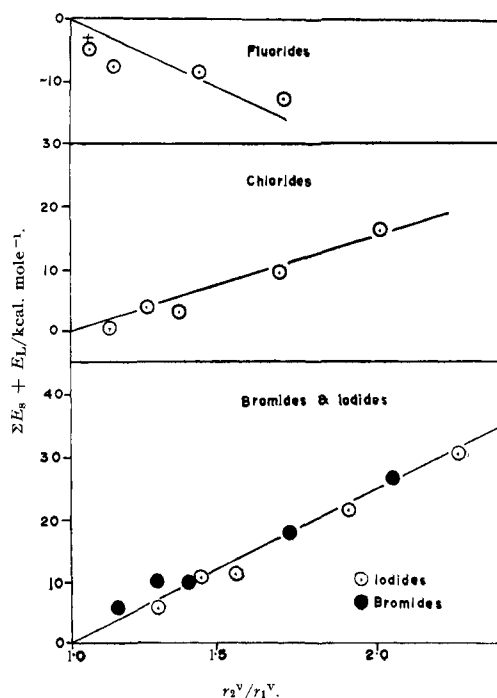
Fig. 1.—Relation between lattice energy of crystals and self energy of gaseous ions for alkali halides. [r_1^v, r_2^v van der Waals radii of gaseous cation and anion, from reference 1. The point (a cross) for CsF is plotted against r_1^v/r_2^v instead of r_2^v/r_1^v, since in this case the cation is larger than the anion.]
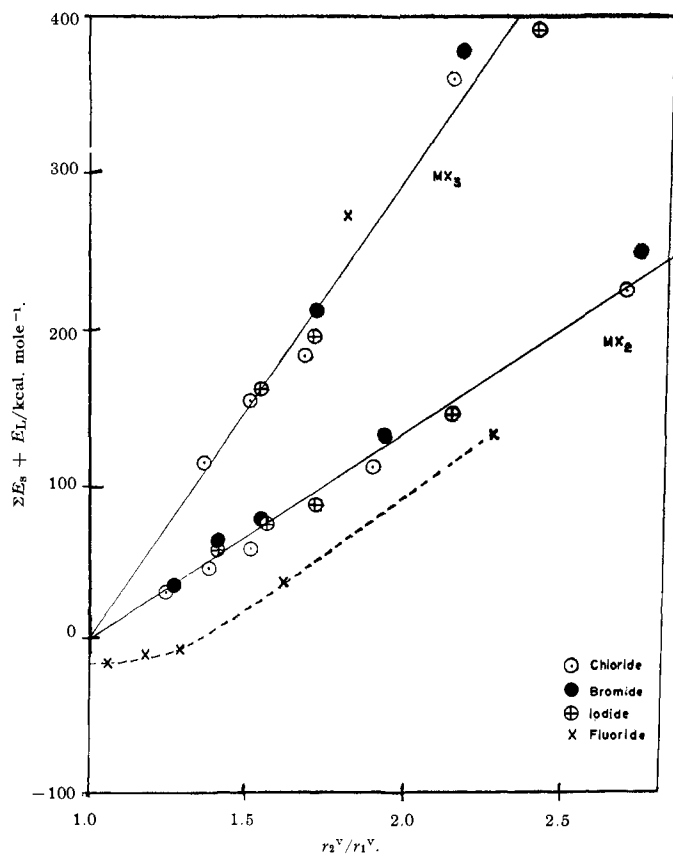

Fig. 2.—Relation between lattice energy of crystals and self energy of gaseous ions for halides of di- and trivalent cations of the noble gas structure.

lattice energies at 298°K. are listed in Table I (column b) for all the halides of uni-, di-, and trivalent cations of the noble gas structure for which the experimental data are available.

Relation between Lattice Energies and Self Energies of Gaseous Ions.

—The electrostatic self energy of 1 mole of gaseous ions of charge ze is

$$E_s = \frac{N}{2}\frac{z^2e^2}{r^v} = \frac{166.0z^2}{r^v}\text{kcal. mole}^{-1}\text{ Å.} \qquad (3)$$

where r^v is the appropriate "equivalent electrostatic radius." In a preceding paper[1] it has been shown that the appropriate radius is the van der Waals radius of the gaseous ion, which is calculable from that of the isoelectronic noble gas atom with the aid of known quantum mechanical screening constants. The value of this characteristic property of the gaseous ion is thus not in any way dependent on measurements of internuclear distances in the ionic crystals considered here. The van der Waals radii and the corresponding electrostatic self energies are listed in reference 1, except for lithium and beryllium ions. For these two ions the method of reference 1 does not lead to unequivocal values for the van der Waals radii. In the present paper. a radius of 1.139 Å. has been arbitrarily assigned to the lithium ion; from this a value of (1.139 × 2.7/3.7) = 0.831 Å. is deduced for the beryllium ion using Slater's[5] screening constant for the 1s-electrons.

The electrostatic self energy of the gaseous ions corresponding to 1 mole of crystal, ΣE_s, is given in Table I, column c. Column d gives the radius ratio of the gaseous ions, r_2^v/r_1^v. where subscript 1 denotes the cation and subscript 2 the anion. It is immediately apparent that *as this ratio approaches unity the self energy of the gaseous ions becomes equal to the crystal lattice energy*, irrespective of crystal structure or valency type.

In Fig. 1 and 2 the quantity ($\Sigma E_s + E_L$) is plotted against the radius ratio. Fluorides show anomalous behavior, but for the other halides a good linear relationship exists. For the 3:1 and 2:1 salts, a single line fits all the chlorides, bromides, and iodides of each class, while for the alkali halides the bromides and iodides fit a single line, and the chlorides require a line of lower slope. It follows that for each of these classes of salts the lattice energy is given by the equation

$$E_L = -\Sigma E_s^v + \beta\left(\frac{r_2^v}{r_1^v} - 1\right) \qquad (4)$$

where β has the values

MX₃	$\beta = 297$ kcal. mole^{-1}
MCl₂, MBr₂, MI₂	$\beta = 132$ kcal. mole^{-1}
MCl	$\beta = 15$ kcal. mole^{-1}
MBr, MI	$\beta = 25$ kcal. mole^{-1}

Discussion

The first fact to be explained is the accurate equality of the (negative) lattice energy and the gaseous ion self-energy for the case of crystals where the cation and anion have equal gaseous van der Waals radii. This is evident from Fig. 1 and 2; it is perhaps open to a little doubt in the case of fluorides, but even with these the amount by which the intercept at $r_2^v/r_1^v = 1$ falls below zero is only 1 or 2% of the lattice energy. A simple explanation suggests itself if we examine the detailed electron density contours of ions in the sodium chloride crystal published, in 1955, by Witte and Wölfel.[6] These workers succeeded by a refined X-ray technique in obtaining contours down to the low density of 0.2 electron Å.$^{-2}$; Fig. 3a is a copy of this lowest contour. It is evident that the outer regions of the electron distributions of the ions are considerably distorted from spherical shape. It would be quite reasonable to say that if the ions had been of equal size, they would have

(6) H. Witte and E. Wölfel, *Z. physik. Chem.* (Frankfurt). **3**, 296 (1955) (especially p. 317).

distorted into polyhedra in complete mutual contact; this picture is confirmed by the fact that the molar volume of all the crystals considered here is less than (or in one or two cases practically equal to) the volume of the gaseous ions calculated from their van der Waals radii. Now the model we are using for the gaseous ion is essentially that of a conducting sphere, and the corresponding model in the crystal would be one of such spheres deformed into polyhedra by the crystal field. For spheres of equal size, complete mutual contact could readily occur; but of course the "conductors" cannot discharge each other because of the quantal stability of their closed (sp) shells. Nevertheless, the classical electrostatic energy of such a system is zero. This is readily seen by considering the general expression for the electrostatic energy of a system of charged conductors

$$E = \frac{1}{8\pi} \int_V \mathbf{R}^2 dV \qquad (5)$$

where $\mathbf{R}$ is the electrical field intensity and the integral is taken *over all the space V outside the conductors*. If the crystal is regarded as a system of conductors in contact, with no voids between them, *there is no space outside the conductors*, and the integral in 5 is therefore zero. This argument of course neglects the ions at the surface of the crystal, the contribution of which to the lattice energy can be made negligible by considering a large enough crystal. (Incidentally, this approach offers an immediate explanation of the enhanced solubility of very small crystals.) It thus appears that the lattice energy for the hypothetical case where the cation and anion have exactly equal van der Waals radii is simply the negative of the self energy of the gaseous ions and can be accurately calculated without appeal to data on the crystal, such as its structure, lattice parameters, compressibility, etc. This strange situation does not of course imply that the established Born–Mayer–Madelung method is wrong, but does indicate that it may be unnecessarily complicated. The writer has never been convinced that it is correct to calculate the contribution of the more remote ions to the Madelung term in the lattice energy using a dielectric constant of unity, for the lines of force from such ions to the central lattice site have to pass through other ions, and these are just as much entitled to have a dielectric constant as are other forms of matter; their refractive index is certainly not unity. Perhaps then the relatively large overlap, dipole, and quadrupole terms of the Born–Mayer treatment are merely a rather difficult way of compensating for the absence of a dielectric constant in the Madelung term.

The present approach thus seems to account for the whole of the lattice energy as electrostatic energy when the ions are of equal size. It is tempting to generalize this conclusion to the case of ions of unequal size, and the values of the coefficient β in eq. 4 give a hint as to how this might be done. Considering the chlorides, bromides, and iodides of the bivalent and trivalent metals, the slopes of the lines in Fig. 2 are precisely proportional to the squares of the cation valency; we can write

$$\beta = \alpha(Nz_1{}^2e^2/2) \qquad (6)$$

where α is a parameter with the dimensions of a reciprocal length, having the fixed value of 0.2 Å.$^{-1}$ for all these 23 salts. Equation 4 may now be written

$$E_L + \Sigma E_s{}^v = \frac{Nz_1{}^2e^2}{2} \alpha \left[\frac{r_2{}^v}{r_1{}^v} - 1 \right] \qquad (7)$$

Let us suppose that the ions are deformed by the crystal field into similar polyhedra with linear dimensions d_1 and d_2, and that these dimensions are proportional to
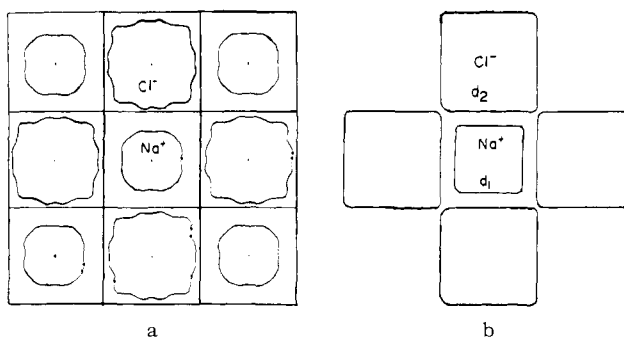

a   b

Fig. 3a.—0.2 electron density contours in sodium chloride (after Witte and Wölfel[6]).

Fig. 3b.—Idealized form of Fig. 3a used as electrostatic model.

the radii of the free ions, so that 7 becomes

$$E_L + \Sigma E_s{}^v = \frac{Nz_1{}^2e^2}{2} (\alpha d_2) \left(\frac{1}{d_1} - \frac{1}{d_2} \right) \qquad (8)$$

The significance of eq. 8 for an electrostatic model is apparent from Fig. 3b, where the actual electron density contours have been idealized to cubes, with the larger cubes in contact along their edges. (In crystals with higher cation coordination numbers than 6, the polyhedra will not be cubes, but this does not matter provided that the cation and anion polyhedra are geometrically similar.) The cation and the adjacent faces of its nearest-neighbor anions thus form a "condenser," the capacity of which will to a good approximation be a constant multiple of that of a spherical condenser of radii d_1 and d_2. We therefore write its capacity as

$$C = \gamma / \left(\frac{1}{d_1} - \frac{1}{d_2} \right) \qquad (9)$$

where γ is a dimensionless constant. Since the charge is z_1e on the cation and $-z_1e$ distributed over the adjacent faces of the surrounding anions, the electrostatic energy per mole is

$$E_c = \frac{Nz_1{}^2e^2}{2\gamma} \left(\frac{1}{d_1} - \frac{1}{d_2} \right) \qquad (10)$$

so that we identify the constant γ of 9 with $1/(\alpha d_2)$ of 8. It is by no means easy to see why γ, which plays the role of a dielectric constant (multiplied by a constant geometrical shape factor), should take the form $\gamma = 1/(\alpha d_2)$, a relation which implies that the effective dielectric constant of the region between the polyhedral limits described around the ions is inversely proportional to the size of the anion. The fact remains, however, that if we make this simple assumption, all that is necessary to give with an accuracy of $\pm 1.2\%$ the lattice energies of the 23 bivalent and trivalent metal salts mentioned is the single parameter $\alpha = 0.2$ Å.$^{-1}$. This is a useful alternative to the standard treatments which require data on the crystal structure, internuclear distances, and compressibilities to give results of scarcely greater accuracy.

The value of α becomes 0.150 Å.$^{-1}$ for the alkali bromides and iodides, and 0.092 Å.$^{-1}$ for the alkali chlorides. The lattice energies calculated by equations are given in column d of Table I. Though the alkali fluorides could be fairly well dealt with by a small negative value of α, the accuracy would be lower than that for the other halides, and Fig. 2 indicates that the model is unsatisfactory for the fluorides. It appears to be most appropriate for highly polarizable anions, and to become more general as the cation charge increases, in that one value of α serves for all the chlorides, bromides, and iodides of the multivalent cations, while a change in α is necessary for the univalent cations.

Since the parameter α gives good values of the crystal energy, it follows that *given α and data for the elements*

only we can calculate the heats of formation of the salts; this is a worthwhile contribution to the theory of chemical bonding. It must be noted, however, that where the cations are multiply charged, the crystal lattice energy can be several times the heat of formation; consequently the 1.2% average error in the lattice energy is considerably magnified if we use the theory to calculate heats of formation from the elements in their usual standard states. This suggests that the free gaseous atoms might be a more practical starting point for considering energies of compounds, rather than such highly unstable ionic species as gaseous Al^{+3}. As might be anticipated, the electrostatic self energies of noble gas cations calculated as proposed by the writer[1] are not greatly different from the total ionization potentials of the gaseous atoms when losing all the electrons outside their closed (sp) shells.

The possibilities of the present treatment were clearly envisaged by Onsager[7] in 1939; I am indebted to a referee for drawing my attention to this important paper. Onsager points out that the "proper energy" of an assembly of "hard" ions is a minimum when ,the surface field intensities of cation and anion are equal, and considers the lattice energy in relation to the self energy of gaseous ions. The principal new feature of the present paper is the recognition that the ion *in vacuo* may reasonably be treated as having a different size and shape from those it has in the crystal, so that the self energy of the gaseous ion is no longer that of a charged sphere of the crystal ionic radius, but that of a larger sphere.

Conclusion

The proposed electrostatic model of ions in the crystal deformed from spheres to polyhedra is remarkably successful, in that it makes possible the calculation of the lattice energies of the chlorides, bromides, and iodides of all the metal cations of the noble gas structure from only three values of the parameter α, with an accuracy averaging $\pm 1\%$; and it requires no information about the crystal, the main contribution to the lattice energy coming from the loss of the self energy of the gaseous ions which is calculable *a priori* from data on the noble gas atoms only.

A curious feature of the present treatment is that it is apparently unnecessary to make a separate allowance for the energy required to compress and deform the ions. In the hypothetical case where the cations are the same size as the anions, the model requires only that in the final crystal they should deform into complete mutual contact; provided this occurs it is immaterial to the energy calculation whether they also

(7) L. Onsager, *J. Phys. Chem.*, **43**, 189 (1939).

undergo a change in volume. In this model we are considering a set of bodies under coulomb interactions, and we find that we can correctly calculate the total energy of the system by considering only the coulombic energy. If we shift our energy zero so as to reckon from the infinitely dilute gaseous ions as zero, the total energy of an ion in the crystal is negative, $W = -E_s^v$. According to the virial theorem, the mean potential energy is $2W$, and the mean kinetic energy is $-W = +E_v^s$. Now where is this kinetic energy? It is certainly not in the zero-point vibrational energy of the lattice, for this is only a fraction of a kilocalorie per mole. It must therefore be in the electrons within the ions. To increase the kinetic energy of an electron, it is necessary to reduce the space in which it moves. In the present case this means that the ions have to deform and become smaller, in order that the kinetic energy of the electrons shall remain equal and opposite to the total energy of the system. The final size and shape of the ions is thus determined by the condition that the increase in the kinetic energy of their electrons should be equal and opposite to the loss in total energy, which can be calculated from the electrostatic model. The appropriate quantum theoretical calculations to determine the final crystal dimensions would be prohibitively difficult, at least to the writer, but the calculation of the total energy change is quite elementary by the methods used here. The conclusion is that the energy of compression and deformation does not have to be taken into account provided that, as here, we can calculate the total energy of the initial and final states from electrostatic considerations. The compressibility of the crystal under an external applied pressure should be similar to that of the corresponding noble gases when the latter are under such pressure that the ratio

$$\bar{V}_{solid}/r_v^3 \text{ (inert gas)}$$

is the same as the ratio

$$\bar{V}_{solid}/(r_1^{v3} + r_2^{v3}) \text{ (ionic crystal)}$$

Unfortunately the compressibility data for the solid noble gases do not extend to high enough compressions to make a direct comparison possible, but if the compressibility of solid argon, known up to 4000 atm., is plotted against $\bar{V}/r_v^3$, the point for potassium chloride at ordinary pressure falls on a natural extrapolation of the curve.