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The lattice energies of NH_4F and of the CsCl-type lattices of the other ammonium halides are computed by the method of Born and Mayer, assuming ionic crystals with a van der Waals potential. The calculations appear to be quantitatively satisfactory for the chloride, bromide and iodide. The method fails, however, for the asymmetrical fluoride lattice, and another method is employed. The theoretically calculated lattice energies in kilocalories are, NH_4Cl, 161.6; NH_4Br, 154.0; NH_4I, 145.5. From these lattice energies by means of a thermal cycle the energy change at $0°K$ of the reaction $NH_{3gas}+H^+_{gas}{\rightarrow}NH_4^+_{gas}$, which may be called the proton affinity of ammonia, is found to be -206.4 kcal. With this proton affinity and the same cyclic process the lattice energy of NH_4F is calculated to be 191.4 kcal.

INTRODUCTION

THE ammonium halides, with the exception of the fluoride, are dimorphic, crystallizing in the CsCl-type lattice at low temperatures and in the rocksalt-type lattice at elevated temperatures. The fluoride possesses a Wurzite-type lattice. The interest in the anomalous behavior of the ammonium halides has created during recent years a considerable literature describing the physical properties of these salts. These data now make it possible to evaluate the lattice energies with some degree of accuracy. This calculation is carried out here following the method of Born and Mayer.[1] Reference should be made to their paper since the detailed equations and notations will not be given here. The lattice energies, U, of these uniunivalent ionic crystalline salts, namely the energy changes at $0°K$ of the reactions $NH_4X_{cryst.}{\rightarrow}NH_4^+_{gas}+X^-_{gas}$, are given by

$$-U=\Phi(r_0)=-\frac{\alpha e^2}{r_0}-\frac{C}{r_0^6}-\frac{D}{r_0^8}+B(r_0)+\tfrac{1}{2}h\nu_0. \quad (1)$$

The term varying inversely with the lattice distance, r_0, is the electrostatic energy. The terms varying as r_0^{-6} and r_0^{-8} are, respectively, the dipole-dipole and the quadrupole-dipole contributions to the van der Waals potential. $B(r_0)$ is the repulsive potential and $h\nu_0/2$ is the zero-point energy.

CALCULATION OF THE VAN DER WAALS POTENTIAL

The evaluation of the constants C and D from the polarizabilities, α, and from certain energies, ϵ, of the ions *in the lattice* has been discussed by Mayer.[2] ϵ is an energy corresponding to a weighted average frequency of absorption of the ion in the crystal. The values of ϵ for the negative ions of the ammonium halides are taken to be the same as the values found by Mayer[2] for the negative ions of the rubidium halides. The values used for the matrix elements, Q_{00}^2, of the negative ions are the average values found by Mayer[2] for the negative ions of the alkali halides. The polarizabilities, α, of the negative ions are then calculated from the relation

$$Q_{00}^2=(3/2)(\alpha\epsilon/e^2). \quad (2)$$

The energy, ϵ, of the positive ammonium ion is given the value 90 percent of the ionization potential (the potential required to produce a doubly charged ion) of the gaseous ammonium ion. This ionization potential of NH_4^+ is estimated to be 31.7 volts by proportion from the ionization potentials of its electronic isomers CH_4, Na^+ and Ne, which are, respectively, in volts, 14.5,[3] 47.0[4] and 21.47.[4] The polarizability,

[1] M. Born and J. E. Mayer, Zeits. f. Physik **75**, 1 (1932).

[2] J. E. Mayer, J. Chem. Phys. **1**, 270 (1933).

[3] T. R. Hogness and H. M. Kvalnes, Phys. Rev. **32**, 942 (1928).

[4] R. F. Bacher and S. Goudsmit, *Atomic Energy States*. McGraw-Hill, New York, 1932.

α, of the ammonium ion in the lattice is calculated from its molar refractivity given by Wulff and Cameron[5] as 4.30. The matrix element, Q_{00}^2, of the ammonium ion is then computed by means of Eq. (2).

The sums of the polarizabilities of the negative and positive ions, $\Sigma\alpha$(calc.), Table III, row 9, have been compared with the experimental values, $\Sigma\alpha$(yellow), row 10, calculated from the indices of refraction, n_D^{25}, for yellow light.[5] The experimental values of $\Sigma\alpha$(yellow) will be lower than those which would be calculated were the index of refraction extrapolated to $\lambda = \infty$, because of the infrared vibrations of the ammonium ion. An estimated value of $\Sigma\alpha(\lambda = \infty)$, calculated from the dielectric constants[6] measured at radiofrequencies, is given in row 11.

The electron numbers, p, of the ions, which are needed to compute D, are taken as the geometric mean of the number of outer electrons, assumed here to be 8 for all ions, and the value calculated from the energy, ϵ, and from the polarizability, α, by the method of Herzfeld and Wolf.[7] The lattice constants S_6', S_6'', S_8' and S_8'', needed in the calculation of C and D, and the Madelung constant, α, needed in the calculation of the electrostatic energy, are given in Table I. These

TABLE I. *Lattice constants.*

Crystal type	Wurzite	CsCl	Crystal type	Wurzite	CsCl
α (Madelung constant)	1.638	1.763	S_8''	0.253	2.148
S_6'	4.354	8.709	a	1.633	1.155
S_6''	0.762	3.545	M	4	8
S_8'	4.104	8.208	M'	12	6

constants as given for the Wurzite-type lattice are in reality those for the very slightly different Zincblend-type lattice. This approximation introduces no error in the final results, however, since it will be shown later that the lattice energy of NH_4F must be calculated by a different method.

[5] P. Wulff and H. K. Cameron, Zeits. f. physik. Chemie **B10**, 347 (1930).

[6] *International Critical Tables*, Vol. VI, p. 99.

[7] K. F. Herzfeld and K. L. Wolf, Ann. d. Physik **78**, 195 (1925).

THE REPULSIVE POTENTIAL AND THE LATTICE ENERGY

To calculate the repulsive potential, $B(r_0)$, it is necessary to approximate the ionic radii. In Table II the lattice distances r_0, the distance

TABLE II. *Rocksalt-type lattice distances.*

Salt	$r_0 \times 10^8$ cm	Salt	$r_0 \times 10^8$ cm
NH_4Cl	3.266	RbCl	3.267
NH_4Br	3.45	RbBr	3.427
NH_4I	3.622	RbI	3.662

between the centers of closest ions, of the NaCl-type lattices of the ammonium and rubidium halides are compared. These lattice distances, taken from the *Strukturbericht*,[8] agree closely, and hence the ionic radius of the ammonium ion is taken to be the same as that of the rubidium ion. The ionic radii given in Table III, rows 22 and 23, are taken from a paper of Huggins and Mayer.[9]

The various steps in the calculation of the repulsive potentials and of the lattice energies are given in Table III. The values in parenthesis are averages of the values for NH_4Cl and NH_4Br. The compressibility data are computed from the measurements of Bridgman.[10] The thermal coefficients of expansion are from the work of Simon and Bergman.[11] Both data are for atmospheric pressure and 273°K. The lattice distances, r_0, as determined from x-ray measurements[8] and as calculated from densities,[5] are given in Table III, rows 20 and 21, respectively. The x-ray values are used here to calculate the lattice energies, except in the case of NH_4F where the density value is used since the x-ray value appears to be of doubtful accuracy. The values of r_0 given for NH_4F represent weighted means since this crystal is so deformed that one of the four neighbors of any ion is closer than the other three. The constants a, M and M', needed in the calculation of the repulsive poten-

[8] P. P. Ewald and C. Hermann, *Strukturbericht 1913–1928*, Akad. Verlagsgesellschaft, Leipzig, 1931.

[9] M. L. Huggins and J. E. Mayer, J. Chem. Phys. **1**, 643 (1933).

[10] P. W. Bridgman, Phys. Rev. **38**, 182 (1931).

[11] F. Simon and R. Bergman, Zeits. f. physik. Chemie **B8**, 255 (1930).

TABLE III. *Calculation of the lattice energies.*

	Salt	NH$_4$F	NH$_4$Cl	NH$_4$Br	NH$_4$I
1	Salt	NH$_4$F	NH$_4$Cl	NH$_4$Br	NH$_4$I
2	Crystal type	Wurzite	CsCl	CsCl	CsCl
3	Q_{00}^2 (neg. ion) $\times 10^{16}$ cm^2	1.44	3.40	4.08	5.27
4	Q_{00}^2 (pos. ion) $\times 10^{16}$ cm^2	5.08	—	—	—
5	ϵ (neg. ion) $\times 10^{12}$ ergs/molecule	18.5	15.7	13.8	12.0
6	ϵ (pos. ion) $\times 10^{12}$ ergs/molecule	45.3	—	—	—
7	α (neg. ion) $\times 10^{24}$ cm^3	1.18	3.29	4.49	6.66
8	α (pos. ion) $\times 10^{24}$ cm^3	1.70	—	—	—
9	$\Sigma\alpha \times 10^{24}$ (calc.) cm^3	2.88	4.99	6.19	8.36
10	$\Sigma\alpha$(yellow) $\times 10^{24}$ (exp.) cm^3	2.83	4.96	6.22	—
11	$\Sigma\alpha(\lambda = \infty) \times 10^{24}$ (exp.) cm^3	—	9.09	10.8	—
12	$c_{++} \times 10^{60}$ ergs cm^6	98	—	—	—
13	$c_{--} \times 10^{60}$ ergs cm^6	19	127	208	399
14	$c_{+-} \times 10^{60}$ ergs cm^6	40	98	121	161
15	$d_{++} \times 10^{76}$ ergs cm^8	150	—	—	—
16	$d_{--} \times 10^{76}$ ergs cm^8	24	266	510	1192
17	$d_{+-} \times 10^{76}$ ergs cm^8	55	177	240	363
18	$C \times 10^{60}$ ergs cm^6	217	1251	1597	2286
19	$D \times 10^{76}$ ergs cm^8	248	1898	2681	4423
20	$r_0 \times 10^8$ (from x-rays) cm	2.67	3.342	3.514	3.785
21	$r_0 \times 10^8$ (from density) cm	2.699	3.347	3.508	—
22	$r_- \times 10^8$ cm	1.133	1.503	1.624	1.810
23	$r_+ \times 10^8$ cm	1.294	—	—	—
24	$\beta \times 10^{12}$ (compressibility) barye^{-1}	—	5.76	6.13	—
25	$\beta^{-1}(\partial\beta/\partial T)_p \times 10^4$ degree^{-1}	—	14	9.5	—
26	$\beta^{-1}(\partial\beta/\partial P)_T \times 10^{11}$ barye^{-1}	—	-4.5	-5.3	—
27	$V^{-1}(\partial V/\partial T)_p \times 10^4$ degree^{-1}	—	1.42	1.61	—
28	$(3T/N\beta)(\partial V/\partial T) \times 10^{12}$ ergs/molecule	(1.30)	1.16	1.44	(1.30)
29	$r_0^2[d^2\Phi(r_0)/dr^2] \times 10^{12}$ ergs/molecule	—	99.3	89.2	—
30	$\alpha e^2/r_0 \times 10^{12}$ ergs/molecule	13.81	12.00	11.41	10.60
31	$C/r_0^6 \times 10^{12}$ ergs/molecule	0.56	0.90	0.85	0.78
32	$D/r_0^8 \times 10^{12}$ ergs/molecule	0.09	0.12	0.12	0.11
33	$\tau \times 10^{12}$ ergs/molecule	16.6	17.2	16.0	14.8
34	$\sigma \times 10^{12}$ ergs/molecule	—	170	156	—
35	σ/τ	—	9.87	9.75	—
36	$\rho \times 10^8$ cm	(0.359)	0.347	0.371	(0.359)
37	r_0/ρ calculated	7.52	9.63	9.47	10.54
38	$B(r_0) \times 10^{12}$ ergs/molecule	2.17	1.75	1.65	1.36
39	$\frac{1}{2}h\nu_0 \times 10^{12}$ ergs/molecule	0.20	0.12	0.10	0.08
40	$U \times 10^{12}$ (calc.) ergs/molecule	12.09	11.15	10.63	10.04
41	U (calc.) kcal.	175.2	161.6	154.0	145.5
42	U (thermal cycle) kcal.	191.4	—	—	—

tial, are given in Table I. The values of c_1 and c_2, which give the dependence of the repulsion on the charge, are computed from a theoretical equation of Pauling's[12] assuming 8 electron shell positive and negative ions. These values are 1.25 and 0.75, respectively. The small zero-point energy is easily estimated.

The values of the lattice energies in ergs per molecule and in kcal. calculated by means of Eq. (1) are tabulated in Table III, rows 40 and 41. The lattice energy thus found for NH$_4$F is more than 16 kcal. too small. The error is due to the fact that Eq. (1) holds only for perfectly

symmetrical crystals, whereas NH$_4$F is deformed or asymmetrical. It is obvious for reasons of stability that the nature of the forces producing the asymmetry must be such as to increase the lattice energy above that of a symmetrical crystal of equal lattice distance. The correct lattice energy of NH$_4$F, as given in Table III, row 42, is calculated in the next section by using a thermal cycle involving the average proton affinity of ammonia found from the lattice energies of the other ammonium halides.

THE PROTON AFFINITY OF AMMONIA

In Table IV are given the energies of the reactions used to calculate the energy change at 0°K of the reaction $NH_{3gas} + H^+_{gas} \rightarrow NH_4^+_{gas}$, which may be called the proton affinity of ammonia. The lattice energies are those of the salts calculated in Table III, and are the energies of the indicated reaction at 0°K. The heats of formation of the crystals are taken from the *International Critical Tables*, as are also the heats of formation of ammonia and of the halogen gaseous atoms. The heat of dissociation of fluorine is from the work of von Wartenberg and Taylor.[13] The energy changes of the crystals between 291°K and 0°K are calculated by integrating the heat capacities measured by Simon, von Simson and Ruhemann.[14] The small energy changes of the gases for this temperature change are estimated. The electron affinities of the halogen atoms are taken from a paper by Mayer and Helmholz[15] where they were calculated from the lattice energies of the alkali halides. The sum of the ΔH's of all of the first eleven reactions gives the ΔH, which at 0°K is the proton affinity of ammonia. The value in parenthesis in the NH$_4$F column is the average value of the proton affinity of ammonia found from the other three halides. From this average value of 206.4 kcal. the ΔH of the first reaction, or the lattice energy of NH$_4$F, is found to be 191.4 kcal.

[12] L. Pauling, Zeits. f. Krist. **67**, 377 (1928).

[13] H. v. Wartenberg and J. Taylor, Goett. Nachr., Math.-phys. Kl., p. 119 (1930).

[14] Simon, v. Simson and Ruhemann, Zeits. f. physik. Chemie **A129**, 339 (1927).

[15] J. E. Mayer and L. Helmholz, Zeits. f. Physik **75**, 19 (1932).

TABLE IV. *Calculation of the proton affinity of NH_3 and the NH_4F lattice energy. ΔH in kilocalories of the reactions.**

Reaction		NH_4Cl	NH_4Br	NH_4I	NH_4F
$NH_4X_{cr.} \rightarrow NH_4{}^+{}_g. + X^-{}_g.$	0°K	161.6	154.0	145.5	191.4
$NH_4X_{cr.}$ 291°K$\rightarrow NH_4X_{cr.}$ 0°K		-3.6	-3.8	-5.0	-2.7
$\frac{1}{2}N_{2g.} + 2H_{2g.} + \frac{1}{2}X_{2s.s.} \rightarrow NH_4X_{cr.}$	291°K	-75.1	-64.7	-48.5	-111.7
$NH_{3g.} \rightarrow \frac{1}{2}N_{2g.} + \frac{3}{2}H_{2g.}$	291°K	11.0	11.0	11.0	11.0
$H_g. \rightarrow \frac{1}{2}H_{2g.}$	291°K	-51.0	-51.0	-51.0	-51.0
$X_g. \rightarrow \frac{1}{2}X_{2s.s.}$	291°K	-28.8	-26.7	-25.5	-31.8
$NH_{3g.}$ 0°K$\rightarrow NH_{3g.}$ 291°K		2.3	2.3	2.3	2.3
$H_g.$ 0°K$\rightarrow H_g.$ 291°K		1.4	1.4	1.4	1.4
$X_g.$ 0°K$\rightarrow X_g.$ 291°K		1.4	1.4	1.4	1.4
$H_g. \rightarrow e^- + H^+{}_g.$	0°K	-312.0	-312.0	-312.0	-312.0
$X^-{}_g. \rightarrow X_g. + e^-$	0°K	86.5	81.5	74.2	95.3
Sum $= NH_{3g.} + H^+{}_g. \rightarrow NH_4{}^+{}_g.$	0°K	-206.3	-206.6	-206.2	(-206.4)

* Subscripts, cr. indicate crystal; s.s., standard state; and g., gas.

The values found here for the lattice energies and the proton affinity may be in error by as much as 3 kcal. due to uncertainties in the lattice distances and compressibilities.

DISCUSSION OF THE RESULTS

Two references concerning the proton affinity of ammonia have been found in the literature. By means of a similar cyclic process van Arkel and de Boer[16] find a proton affinity of 209 kcal., which is in good agreement with the value found here. The agreement is fortuitous, however, since they employ a lattice energy of 148 kcal. for NH_4Cl. This lattice energy is 14 kcal. less than the one found in this paper and must surely be in considerable error. By the method of molecular orbitals Mulliken[17] obtains an ammonia proton affinity of 9.0 volts or 207 kcal., again in good agreement with the value found here.

The good agreement obtained between the ammonia proton affinities deduced from the lattice energies of the ammonium halides is regarded as support for the accuracy claimed in the lattice energy calculations. It also shows that the ammonium halides are definitely ionic crystals to which the equations of Born and Mayer quantitatively apply.

The author is greatly indebted to Professor Joseph E. Mayer for suggesting the foregoing problem, and is very grateful to him for the advice received in working it out.

[16] A. E. van Arkel and J. H. de Boer, Physica **7**, 354 (1927).

[17] R. S. Mulliken, J. Chem. Phys. **1**, 492 (1933).