Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Polarization of Ions and Lattice Distances

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THE considerable deviations from additivity shown by the molar refraction of inorganic compounds (cf. Fig. 1a) have been considered[1] in the main as a result of two effects.

(1) The tightening of the anion in the field of the cation.
(2) The loosening of the cation in the field of the anion.

The magnitude of these changes depends on the field strength of the polarizing particle and on the polarizability of the other. A few data concerning the relative polarizabilities of the ions and molecules involved in the discussion of this and the next two letters will be helpful. The values given represent the refraction (D line) in cc/mole; in the case of the complex ion ClO_4^-, the refraction per single oxygen octet is taken as the measure of the polarizability, for the unsymmetrically bonded NO_3^- somewhat more than $\frac{1}{3}$ of its refraction. The values for Na^+ to Cs^+ lie between 0.5 and 6.5, for F^- to I^- 2.5 to 19, $O^=$ to $Te^=$ 7 to 41, H_2O 3.7, $\frac{1}{4}$ ClO_4^- 3.3, NO_3^- ca. 4, H^- ca. 7, OH^- 4.8, Ag^+ 4.8.

The radius of particles of similar structure being assumed proportional to the cube root of the molar refraction, one would expect the interionic distances to show similar although smaller deviations from additivity due to polarization.

Until now, the interionic distances of only the silver[2] and thallous halides[3] when compared with alkali halides were recognized as showing deviations from additivity in

the expected direction. Both cations are not of the noble gas type, and it is of importance to show that the effect can be found also when only ions of noble gas structure are involved. All compounds[4] in Table I of the type AB have the sodium chloride, those of the type AB_2, the fluorite structure.

As the three sets of differences show, we have in all cases systematic deviations from additivity which for $H^- - F^-$ amount to 8 percent of the lattice distance. As the anions appear to be of nearly equal size for the Li and Ca compounds it is not possible to explain these deviations from additivity by the "radius ratio"[5] effect of rigid ions.

The difference between oxide and fluoride and between hydride and fluoride becomes larger from Li to K, i.e., with decreasing field strengths of the alkali ion, and the same holds for the comparison of the oxides and fluorides of the doubly charged cations. As the polarizability of $O^=$ and of H^- is considerably larger than that of F^-, one has to conclude that the decrease of the size of the anion in the field of the cation contributes distinctly to these deviations from additivity. Furthermore, the fact that the value of $H^- - F^-$ has a maximum for Rb shows that a second effect is involved which can be interpreted as a stronger loosening action of the F^- compared with the H^- on the more easily polarizable cations.

We can now arrive at some new conclusions comparing the lattice distances of silver and sodium salts. (Table II.)

The great deviations from additivity shown by the halides were explained[6] by the stronger polarizing action
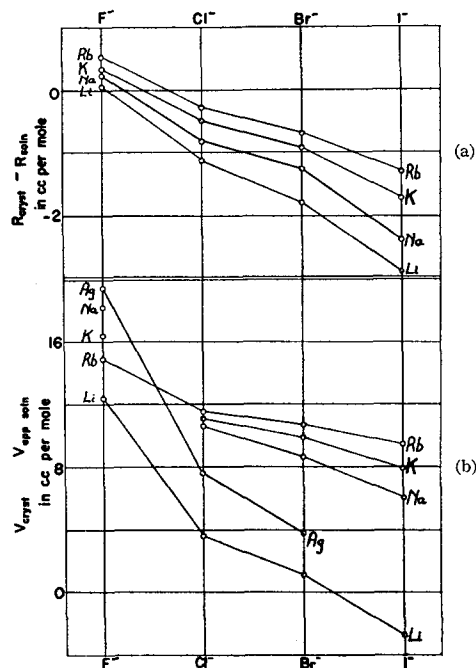
FIGS. 1a and 1b. Differences between the molar volumes and molar refractions of solids and the corresponding apparent quantities in aqueous solution.

TABLE I. *Interionic distances in A.**

	Li	Na	K	Rb	Cs	Ca	Sr	Ba
O	2.00₀	2.40₃	2.78₆			2.40₁	2.57₃	2.76₅
O⁼−F⁻	−0.01₀	0.09₃	0.12₀			0.04₁	0.07₀	0.08₇
F	2.01₀	2.31₀	2.66₆	2.82	3.00₄	2.36₀	2.50₃	2.67₈
H⁻−F⁻	0.03₂	0.13₀	0.18₄	0.20	0.18₄			
H	2.04₂	2.44₀	2.85₀	3.02	3.18₈			

	Li	Na	K	Rb	Cs	Ca	Sr	Ba
O	2.00_0	2.40_3	2.78_6			2.40_1	2.57_3	2.76_5
O⁼−F⁻	-0.01_0	0.09_3	0.12_0			0.04_1	0.07_0	0.08_7
F	2.01_0	2.31_0	2.66_6	2.82	3.00_4	2.36_0	2.50_3	2.67_8
H⁻−F⁻	0.03_2	0.13_0	0.18_4	0.20	0.18_4			
H	2.04_2	2.44_0	2.85_0	3.02	3.18_8			

*From the best determinations according to the *Strukturbericht*, Vols. I–IV, 1913–1936.

TABLE II. *Lattice distances in A.*[†]

	F	Cl	Br	I	ClO₄
Ag	2.452	2.773	2.886	(3.05)	3.5₉
Ag⁺−Na⁺	+0.132	−0.041	−0.095	−0.18	−0.0₄
Na	2.320	2.814	2.981	3.231	3.5₄

	F	Cl	Br	I	ClO_4
Ag	2.452	2.773	2.886	(3.05)	3.5_0
Ag^+-Na^+	+0.132	−0.041	−0.095	−0.18	-0.0_4
Na	2.320	2.814	2.981	3.231	3.5_4

† All the values (see footnote to Table I) apply to sodium chloride structure, which $AgClO_4$ and $NaClO_4$ have at high temperatures above 155° and 314°C, respectively. (For the new value for AgF we are indebted to Professor L. S. Ramsdell.)

of the silver ion, which does not possess the rare gas structure and the increasing polarizability from F^- to I^-. However, the difference Ag^+-Na^+ for the perchlorates is also considerably more negative than that for the fluorides, in spite of the small polarizability of ClO_4^- and its greater separation from Ag^+. This cannot be explained by "anion contact." Thus it appears that the larger distance in AgF compared with NaF is mainly due to the loosening effect of the small F^- on the more easily polarizable Ag^+. In cases where polarization effects can be neglected, one can consider the size of Ag^+ and Na^+ as nearly equal, or probably that of Ag^+ as a little larger.

[1] K. Fajans and G. Joos, Zeits. f. Physik 23, 1 (1924). Cf. the list of later papers, e.g., K. Fajans, Zeits. f. physik. Chemie B24, 103 (1934); A. Kruis, ibid. 34, 82 (1936).
[2] K. Fajans, Naturwiss. 11, 165 (1923).
[3] V. M. Goldschmidt, Norske Videns.-Akad., Oslo, No. 8, 72 (1927).
[4] Concerning the hydrides, cf. E. Zintl and A. Harder, Zeits. f. physik. Chemie B14, 265 (1931).
[5] Cf. K. Fajans and K. F. Herzfeld, Zeits. f. Physik 2, 317 (1920); L. Pauling, J. Am. Chem. Soc. 49, 765 (1927).
[6] Cf., e.g., K. Fajans, Cornell lectures, 1931.

Molar Volume, Refraction and Interionic Forces

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THE data in the preceding letter show the important influence of the polarization of the ions on lattice distances and give a new support to the conclusions arrived at by the study of the deviations of molar refraction from additivity which were explained on the basis of the polarization (deformation) of the electronic systems.

Th. Neugebauer[1] in a series of papers developed a wave mechanical theory of these influences. His conclusions agree in all respects with those derived from the experimental evidence and give a better theoretical understanding of the relations involved.

The view is generally accepted that when an anion and cation combine to form a molecule or crystal, their electronic systems interpenetrate each other. As is implied in the calculations of Neugebauer and clarified by very valuable discussions with Professor Roger H. Gillette, this interpenetration is equivalent to an introduction of a positive charge into the electronic system of the anion and of a negative charge into that of the cation.

From the above we can conclude that the addition of a cation to an anion leads to a diminution not only of the refraction (polarizability) of the anion but also to a contraction of its volume.

How large this effect can be is shown by the fact that the refraction of I^- is 19.2 cc/mole, that of HI is 13.7 cc/mole and that the volume of these particles can, in first approximation, be assumed to be proportional to their refractions.

An increase of the size of a cation is to be expected when it combines with an anion.

In order to test whether the above expectations find confirmation also in the classical case of alkali halides, in Fig. 1b* are plotted the differences between the molar volumes of the solids and the apparent volumes of the salts in infinitely dilute solution. As the latter values are exactly additive within the experimental errors, the pronounced deviations from additivity revealed by Fig. 1b show clearly that they are due to the behavior of the volume of the solid salts. It is not possible to discuss the details in this short letter. It may only be emphasized that the general character of the deviations from additivity is the same as shown in the corresponding Fig. 1a by the molar refractions. Lithium iodide, in which we have to expect the strongest tightening of the anion, appears at the bottom of both figures; the fluorides, in which a loosening of the cation is expected, are at the top of the figures.

The regularities of the Figs. 1a and 1b show some differences which are in part due to the much stronger influence of the ions on the volume of the solvent than on its refraction.

A similar figure resulted, in an investigation with Mr. Norman Bauer, by plotting the differences between the corresponding values of the molar dispersion of light, (R_D-R_∞), of the alkali halides. The relative deviations from additivity are, in the case of dispersion, generally stronger than for the refraction.

The deviations from additivity of the volumes of solid alkali halides shown by Fig. 1b were demonstrated long ago,[2] but were not understood at that time, by the method used in the above letter in discussing lattice distances; e.g., the difference between the molar volumes of iodides and bromides increases from 7.88 cc for lithium to 10.44 cc for rubidium. However, the difference in lattice distances in this case diminishes from 0.262A for the lithium salts to 0.227A for the rubidium salts. The explanation of this apparent contradiction follows simply from mathematical properties of the differences of distinctly different numbers and differences between their cubes. For the hydrides and fluorides of Li to Rb both the differences in volume[3] and distance vary in the same direction due to the approximate equality of the corresponding values. So it is not necessarily an indication of the ions behaving as rigid spheres when the lattice distances sometimes do not show any appreciable deviations from additivity.

* See preceding letter.
[1] Th. Neugebauer, Physik. Zeits. 94, 655 (1935); 99, 687 (1936); Hungarian Acad. Sci. 54, 337 (1936).
[2] K. Fajans and H. G. Grimm, Zeits. f. Physik 2, 299 (1920).
[3] Cf. Wilhelm Biltz, *Raumchemie der festen Stoffe* (Leopold Voss, Leipzig, 1934), p. 166.