

## Electronic Structure and Stability of Hydrogen Halides and of Complex Ions $\text{XO}_4$

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(1) It is shown that in the hydrogen halide molecules (internuclear distance  $r_0$ ) the proton penetrates the electronic shell of the anion to a depth which for the simplified case of spherical symmetry can be characterized by the condition: The amount of negative charge beyond the sphere of radius  $r_0$  equals  $-1e$ . (2) From the dipole moments  $\mu = xer_0$  of the hydrogen halide molecules it can be concluded: The wave mechanical distribution of the negative charge of the free halide ions is changed by the introduction of the proton in such a way that the center of gravity of an amount of charge equal to  $-(1-x)e$  is shifted from the halogen nucleus to the proton. The fraction  $(1-x)$  increases with the electronic polarizability of the anion, and would be equal to 1 for an ion of infinitely large polarizability, leading to a completely unpolar type of binding in this case.

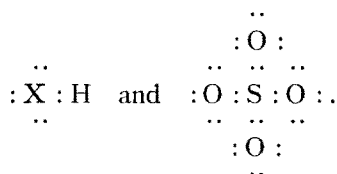
(3) It is shown that for the complex ions  $\text{SiO}_4^{4-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{ClO}_4^-$ , the gradation of the X-O distances and of the molar dispersion can be easily understood from the point of view used in 1924 for the case of the molar refraction: These ions represent the result of the polarization of  $\text{O}^-$  by  $\text{Si}^{4+}$ ,  $\text{P}^{5+}$ ,  $\text{S}^{6+}$ , and  $\text{Cl}^{7+}$ , and the X-O binding in them shows gradual changes toward the unpolar type. (4) It is pointed out that the relatively unstable  $\text{HI}$  and  $\text{ClO}_4^-$  approach the unpolar type of binding more closely than any other of the compounds considered here. The generalization of this connection between instability and the degree of deformation of electronic shells explains why compounds like  $\text{FO}_4^-$  and  $\text{BrO}_4^-$  are unknown.

### INTRODUCTION

THE problem of the electronic structure of chemical compounds has been approached in many more or less different ways. Limiting ourselves here to simple inorganic substances we shall characterize four points of view by mentioning how they describe the structure of the hydrogen halide molecules (HX) and of the sulphate ion.

(a) According to the extreme ionic point of view used by W. Kossel (1916), in HX the proton is attached to the spherical halide ion of definite size; in  $\text{SO}_4^{2-}$  four  $\text{O}^-$  are attached to the  $\text{S}^{6+}$  ion.

(b) In the well-known theory of the covalent bond of G. N. Lewis (1916) one has the formulae



(c) According to the polarization or deformation point of view (especially since 1923<sup>1</sup>), the hydrogen halides or  $\text{SO}_4^{2-}$  can be thought of as the result of interaction between the anion  $\text{X}^-$

or  $\text{O}^-$  with the proton or  $\text{S}^{6+}$ , respectively, and represent examples of a type of binding intermediate between (a) and (b).

(d) From the resonance point of view (especially L. Pauling<sup>2</sup> since 1931), the real HX molecule is considered to be the result of the resonance between two hypothetical extreme forms of HX, one ionic, the other covalent.<sup>3</sup> The Lewis formula for  $\text{SO}_4^{2-}$  is concluded to be unsatisfactory on the basis of the interatomic S-O distance. It is suggested that one should use the old structural valence line formula with two double and two single bonds and for a more precise electronic description to add several (seven are mentioned specifically) of the possible resonating structures (see reference 2, pp. 239-243).

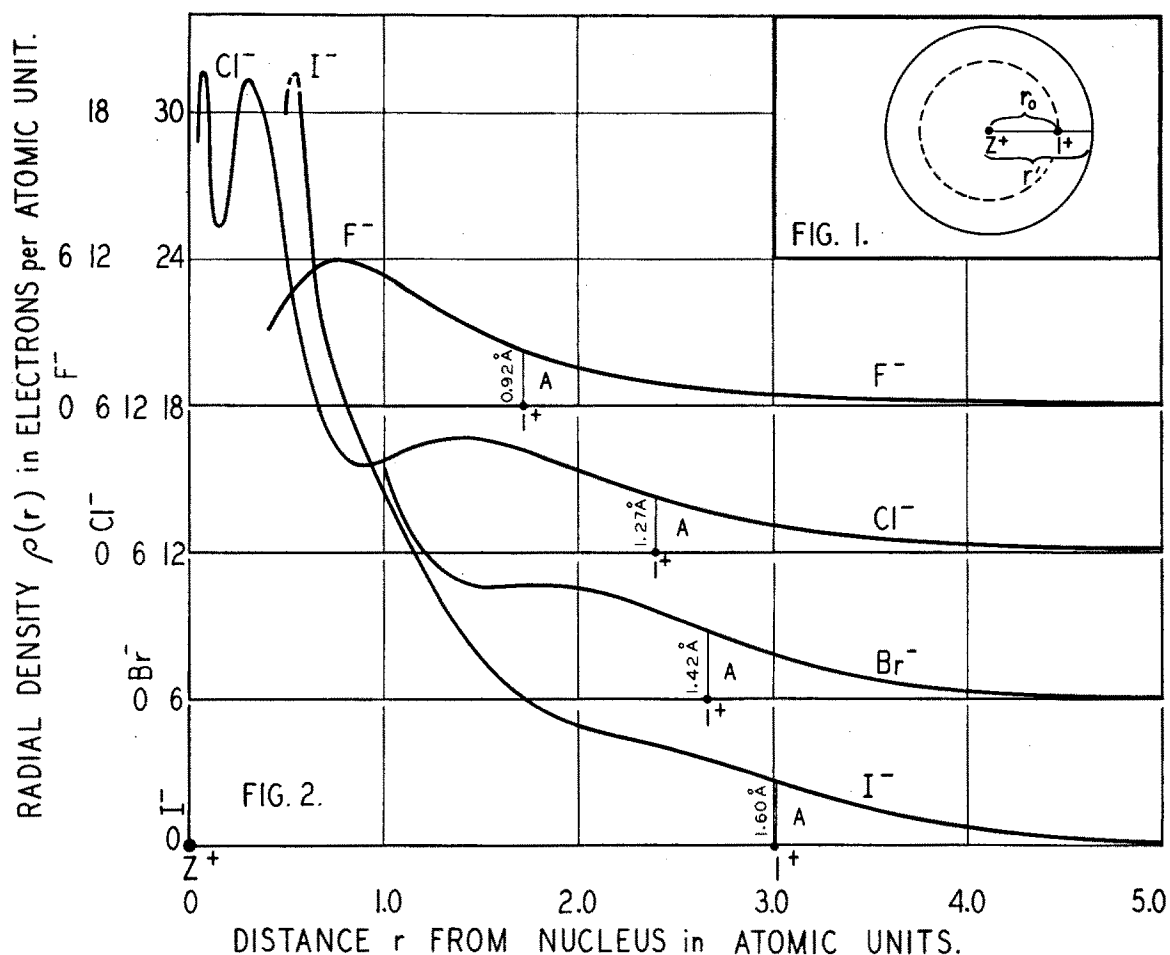
Here we shall extend the former descriptions<sup>4</sup> based on the polarization theory making use of some newer theoretical and experimental results with special emphasis on such points as

<sup>2</sup> See the presentation in L. Pauling, *Nature of the Chemical Bond*, second edition (Cornell University Press, Ithaca, New York, 1940).

<sup>3</sup> In respect to HF, its ionic character is estimated in reference 2, p. 49 to be 60 percent. On p. 297, however, the extreme ionic concept of the H-F bond is supported by the statement that calculations on this basis lead to an excellent agreement with the observed value for the internuclear distance in HF and to a close agreement for the F-F distance in  $\text{HF}_2^-$ . See also Fig. 38-1.

<sup>4</sup> K. Fajans and G. Joos, *Zeits. f. Physik* **23**, 1, 1924. See also reference 1, pp. 21 and 86, and reference 6b.

<sup>1</sup> See the presentation in K. Fajans, *Chemical Forces and Optical Properties of Substances* (Cornell Lectures), (McGraw-Hill Book Company, New York, 1931).



Figs. 1 and 2 show the position of the proton within the electronic shells of halide ions. Figure 1 is for the simplified case of a spherically symmetrical anion of definite radius  $r'$ . Figure 2 gives the wave mechanical electron distribution in the free halide ions, with the proton at the actual internuclear distance  $r_0$  it has in the hydrogen halide molecule.

will be necessary for the discussion of certain open questions in the valence theory, such as the hydrogen bond, boron hydrides, etc.<sup>5</sup>

### 1. HALIDE IONS OF DEFINITE RADIUS

Considering the process  $X^- + H^+ = HX$ , it will be helpful first to use the following simplified models (a) and (b):

(a) The electronic system of the free halide ion (nuclear charge  $+Ze$ ) represents a penetrable sphere of definite radius  $r'$  (see Fig. 1). The spherically symmetrical distribution of the negative charge remains unaltered when the distance  $r$  between proton and nucleus changes

from very large values to the equilibrium distance  $r_0$  in the  $HX$  molecule.

(b) The proton changes the charge distribution of the electronic system; i.e., it polarizes and deforms the anion.

*re* (a): For the free ion the center of gravity of the  $-(Z+1)e$  charge of the electronic system coincides with that of the  $+Ze$  charge of the nucleus. For values  $r \geq r'$ , the full attractive force of the excess charge  $-1e$  is the only force acting on the proton. Thus the latter must penetrate the electronic system. With  $r < r'$  the force becomes smaller because, according to the well-known result of the potential theory, one is led to the conclusion that that part of the negative charge outside the sphere of radius  $r$  does not act on the proton. Therefore, the latter

<sup>5</sup> See K. Fajans and W. M. Spurgeon, 103rd meeting of the Am. Chem. Soc., April 1942, Symposium on the Hydrogen Bond, and papers to follow.

will come to the equilibrium distance  $r_0$  when the charge within the shell between  $r_0$  and  $r'$  is equal to  $-1e$ .

*re* (b): We start with the rigid model (a), fix the position of the proton, and allow the charges of the anion to move. Since by the introduction of the proton into the ion an additional attractive force acts on the electronic system, its volume will diminish. The distance  $r_0$  will also be somewhat different from the case (a) but this question does not need to be considered here. The actual loss of spherical symmetry makes quantitative predictions<sup>6</sup> about the details of the electronic distribution extremely difficult.

## 2. HALIDE IONS WITH WAVE MECHANICAL ELECTRON DISTRIBUTION

Figure 2 brings us somewhat nearer to reality. The curves correspond to the radial electron distribution in the free halide ion;<sup>7</sup> the proton ( $1+$ ) is placed at a distance from the nucleus ( $+Ze$ ) which it actually has in the hydrogen halide molecules. Thus if the halide ion were not polarized by the introduction of the proton, in applying appropriately the result obtained under 1(a) we would have to expect that the charge corresponding to the area  $A$  under the curves for  $r$  values between  $r_0$  and  $\infty$  is  $-1e$ . Instead, one finds that these areas correspond very nearly to  $-2e$  for all four hydrogen halide molecules. Assuming these theoretical distribution curves

<sup>6</sup> a. F. Haber, Verh. d. D. Phys. Ges. **21**, 750 (1919); b. K. Fajans, Zeits. f. Elektrochemie **34**, 502 (1928); c. P. Debye, *Polar Molecules* (The Chemical Catalog Company, 1929), p. 59; d. J. G. Kirkwood, Physik. Zeits. **33**, 259 (1932); e. L. Pauling, J. Am. Chem. Soc. **54**, 988 (1932); f. Th. Neugebauer, Zeits. f. Physik **102**, 305 (1936); g. H. Hellmann and S. J. Pshejtzkij, Acta Physicochemica **7**, 621 (1937).

<sup>7</sup> The values of  $\rho(r)$  in the curve for  $\text{Cl}^-$  are taken from D. R. Hartree and W. R. Hartree, Proc. Roy. Soc. **156**, 59 (1936) who used the well-known method of the self-consistent field; those for  $\text{F}^-$  are based on values of the wave functions which were calculated by D. R. Hartree, Proc. Roy. Soc. **151**, 96 (1935) by a similar method. The curve for  $\text{Cl}^-$  is the more reliable, exchange terms having been included.

The values of  $\rho(r)$  for  $\text{Br}^-$  and  $\text{I}^-$  were calculated on the basis of empirical rules given by J. C. Slater, Phys. Rev. **36** (2), 57 (1930) for the screening constants and effective quantum numbers in his analytical expression for the wave functions. This empirical method is likely to give too small values of  $\rho(r)$  at low electron densities, when compared with the Hartree curves. This is the case for  $\text{Cl}^-$ .

for the free ions to be exact enough, this result means that the charge distribution in all four hydrogen halide molecules is different from that in the free ions. If the spherical symmetry of the electronic system were retained in the halide molecules we could draw the additional conclusion that a charge of approximately  $-1e$  has been shifted from the space beyond  $r_0$  into the region between the two nuclei. For the real (non-spherically symmetrical) case such a quantitative theoretical statement does not seem to be possible at present,<sup>6</sup> and one has to consult the experimental facts concerning the dipole moments and molar refraction in order to obtain more information about the change in the electron distribution due to the proton.

## 3. CHANGE OF ELECTRON DISTRIBUTION BY THE PROTON

With the undisturbed electronic cloud of Fig. 2 the dipole moment of the molecule would be  $\mu = er_0$ ; in reality for HCl, HBr, and HI it is  $\mu = xer_0$ , where  $x$  has the values 0.17, 0.11, 0.05 (see references 6b and 2, p. 46), respectively. One can express this fact by saying either that the dipole length is  $l = xr_0$  or that the positions of the halogen nucleus and the proton, separated by the distance  $r_0$ , represent the center of gravity of the charges  $-xe$  and  $+xe$ . This means, when starting with the picture in Fig. 2, that the center of gravity of the charge  $-(1-x)e$  has been drawn over from the halogen nucleus to the proton.

It can be expected that  $(1-x)$  is closely connected with the polarizability of the halide ion. In Fig. 3, curve  $A$ , the values of  $(1-x)$  are plotted against the molar refraction  $R^8$  of  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ . In addition it is obvious that for a rigid ion ( $R=0$ ) one would have  $(1-x)=0$ , and that within an extremely easily polarizable electronic shell ( $R=\infty$ ) the proton would be completely neutralized; i.e., here  $(1-x)=1$ . The curve allows one to interpolate, giving the value  $(1-x)=0.5 \pm 0.1$  for HF, not known experi-

<sup>8</sup> The  $R$  values for the  $D$  line of the aqueous ions (see K. Fajans and R. Lühdemann, Zeits. f. physik. Chemie **B29**, 150 (1935)) were used in the figure because they are better known than the theoretically more significant  $R$  values for  $\lambda = \infty$  of the gaseous ions.

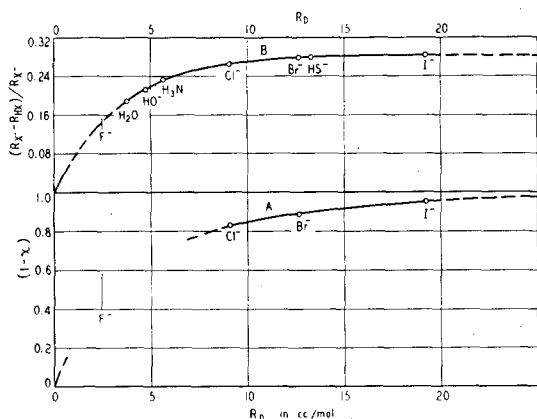


FIG. 3. Curve *A*: the ordinate gives the amount of charge  $-(1-x)e$ , the center of gravity of which is shifted by the introduction of the proton from the nucleus of the free halide ion to the position of the proton in the hydrogen halide molecule. Curve *B*: the ordinate gives the relative change of refraction of  $F^-$ ,  $H_2O$ ,  $\dots$ ,  $I^-$  caused by the introduction of a proton. For both curves, the abscissa is a measure of the polarizability of the initial particle.

mentally. With  $r_0 = 0.92\text{A}$ ,  $\mu = xer_0 = 2.4 \pm 0.5$  debyes.<sup>8a</sup>

From this result it follows that the type of binding in HF is far from that in the extreme case of rigid ions.<sup>3</sup>

#### 4. TIGHTENING OF THE HALIDE IONS BY THE PROTON

It is of interest to note that curve *A* has a form similar to that of curve *B* in Fig. 3, which shows the relative diminution  $-\Delta R/R$  of the molar refraction resulting from the introduction of a proton into anions and neutral molecules (their symbols are given near the points on the curve) as a function of the electronic polarizability ( $R$ ) of the initial particle. This decrease of polarizability, i.e., tightening of the electronic system of anions or neutral molecules, is always found when they combine with an additional positive charge of a cation.<sup>9</sup> Curve *B*, showing this influence in the special case of protons, can

<sup>8a</sup> Note added in proof: This agrees as closely as can be expected with the experimental value (between 2.47 and 2.71 debyes) of the dipole moment of HF in dioxane, communicated by M. E. Hobbs, A. J. Weith, and P. M. Gross at the 103rd meeting of the American Chemical Society, April 22, 1942.

<sup>9</sup> As molar refraction generally goes parallel to size and is sometimes considered as a measure of the "true" volume of a particle, the negative value of  $\Delta R$  is in full agreement with the conclusion reached under 1 and 2 that the extension of halide ions is diminished by the combination with a proton.

be represented<sup>10</sup> by the exponential relation:

$$Q = -\Delta R/R = 0.2859(1 - e^{-0.2848R}). \quad (1)$$

The meaning of relation (1) is that  $-\Delta R/R$ , which can be considered as a measure of the tightening effect, tends towards the limiting value 0.2859 for  $R = \infty$ , which, as the curve indicates, is already closely approached by the easily polarizable iodide ion. The comparison with curve *A* shows that this limiting value of  $Q$  is reached when the field of the proton becomes completely neutralized by the charge drawn from the polarized electronic shell and that hydrogen iodide is close ( $1-x=0.95$ ) to this state of unipolarity of the molecule.<sup>11</sup>

We shall show in Section 6 that this type of unipolarity of binding has some connection with the instability of the corresponding compounds (as shown by HI) but let us first discuss the structure of  $XO_4$  ions.

#### 5. DEFORMATION OF THE OXYGEN OCTET IN IONS $XO_4$

Here, instead of considering the polarizing action of a given particle (proton) on different electronic systems, we can compare the effect which different particles exert on the same electronic system, that of oxygen. The electron affinity of the oxygen atom, i.e., its tendency to complete an octet, is not large enough to make a free gaseous  $O^=$  stable. The process  $O + e^- = O^-$  is exothermic;<sup>12</sup> the second step however is endothermic<sup>13</sup> because of the repulsion between the excess charges of  $O^=$ . However, by combination with positively charged particles like the proton or other cations the electronic shell of  $O^=$  can be stabilized and it is quite appropriate to treat many oxygen compounds as derivatives

<sup>10</sup> K. Fajans, *Zeits. f. physik. Chem.* **B24**, 133 (1934).

<sup>11</sup> It appears surprising that in spite of the great differences in the values  $(1-x)$ , the areas between  $r_0$  and  $\infty$  under the four curves in Fig. 2 are approximately equal, i.e., exceed the charge  $-1e$  by about the same amount for all hydrogen halides. It is difficult to decide how much this is due to the lack of spherical symmetry and how much to uncertainties in the curves in the region of small electron density. (See footnote 7.)

<sup>12</sup> See, e.g., E. E. Hanson, *Phys. Rev.* **48**, 476 (1935); D. R. Hartree, *Trans. Roy. Soc.* **A238**, 229 (1939).

<sup>13</sup> See J. E. Mayer and M. M. Maltbie, *Zeits. f. Physik* **75**, 748 (1932); H. Hellmann and M. Mamotenko, *Acta Physicochimica* **7**, 127 (1937); O. K. Rice, *Electronic Structure and Chemical Binding* (McGraw-Hill Book Company, 1940), p. 101.

of  $O^-$  and the corresponding cations, even in such cases as  $CO_2$  and  $ClO_4^-$  which are usually considered as covalent. But in every case one must consider the changes of the state of the oxygen octet. The molar refraction has proven to be a very sensitive property for such purposes and is only exceeded in this respect by the molar dispersion of light.<sup>14</sup>

The apparent refraction  $R_D$  per single oxygen octet has the values 7.91, 6.81, 6.03, 4.27<sup>15</sup> for the oxides BaO, SrO, CaO, MgO, respectively. This shows that the stronger the electrostatic field of the cation, i.e., the larger its polarizing power, the greater the tightening of the oxygen octet. Therefore, if we consider the complex ions  $SiO_4^{4-}$ ,  $PO_4^{3-}$ ,  $SO_4^{2-}$ ,  $ClO_4^-$  to be formed from  $O^-$  and the corresponding cations  $Si^{4+}$ ,  $P^{5+}$ ,  $S^{6+}$ ,  $Cl^{7+}$  we must expect that refraction, dispersion, and size of the oxygen octet in the complex ions will diminish in the given order, which is that of increasing charge and slightly decreasing size of the small central ion of neon structure. Table I confirms this expectation.<sup>16a</sup> The decrease of refraction between  $SiO_4^{4-}$  and

$ClO_4^-$  per octet is 1.11 cc  $\sim$ 28 percent; the corresponding relative change of the linear dimension X-O (0.12 $\sim$ 8 percent) is, as one would expect, about 3 times smaller. On the other hand, the decrease in molar dispersion between  $SO_4^{2-}$  and  $ClO_4^-$  is 0.014 $\sim$ 22 percent, i.e., relatively about twice as large as the corresponding change in refraction of 0.37 cc  $\sim$ 11 percent.

This tightening effect, as in the case of the hydrogen halides, is the result of the drawing over of the electronic shell of the anion toward the positive charge of the cation and must, therefore, be accompanied by a diminution of the polarity of the X-O binding. Thus these complex ions represent, as do the hydrogen and silver halides, typical transition cases between the extremes of ideal ionic binding and completely unpolar binding (e.g., in  $H_2$ ). In the case of  $ClO_4^-$ , in which the deformation of  $O^-$  is strongest, the binding character is certainly very much nearer to the non-polar type. If one wishes to formulate these ions as covalent structures with both atoms having their octets completed, there is no objection to the Lewis formula,<sup>16</sup> which represents in the correct way the tetrahedral symmetry of these ions (see Introduction).

TABLE I. Interatomic distance, refraction, and dispersion of the oxygen octet in the complex ions  $XO_4$ .

Central cation	$Si^{4+}$	$P^{5+}$	$S^{6+}$	$Cl^{7+}$
X-O in A*	1.60	1.55	1.51	(1.48)
$R_{O^-}$ in cc/mole**	4.42	4.05	3.68	3.31
$R_D - R_\infty$ in cc/mole***			0.071	0.057

\* From Pauling (reference 2, p. 240). The selection of these distances from crystal structure data is not easy to make in view of the uncertainty of the parameter determination in many cases, and because of the influence of the surroundings on these values. The parallelism with the refractometric data indicates, however, that the selection made by Pauling is as satisfactory as possible.

\*\* From K. Fajans and G. Joos, reference 4, p. 38. The value for the silicate ion is based on measurements of A. Heydweiller on  $SiO_3^-$  in which the bonding cannot differ appreciably from that in  $SiO_4^{4-}$ . The values for  $SO_4^{2-}$  and  $ClO_4^-$  differ slightly from those in reference 4 according to newer measurements (see reference 8).

\*\*\* See reference 14.

<sup>14</sup> N. Bauer, Dissertation, University of Michigan, 1941. The results will be published soon; they show that the relative change of dispersion (defined by  $R_D - R_\infty$ ) caused by a given influence on the electronic system is about twice that for the refraction  $R_D$ .

<sup>15</sup> Obtained by subtraction of the values for the gaseous cations (see reference 10, p. 118) from those for the crystals (see reference 6b, p. 511).

<sup>16a</sup> The values of refraction and dispersion are based on measurements of dilute solutions, whereas strictly one should compare gaseous ions. However, a comparison of crystallized salts, e.g., of potassium sulfate and perchlorate (see P. Wulff and D. Schaller, Zeits. f. Krist. **A87**, 64 (1934)) shows the same gradation. This is understandable because in the case of such large anions with small polarizability, one would not expect strong hydration or lattice effects.

## 6. INSTABILITY OF ELECTRONIC SYSTEMS

It is noteworthy that the smallest polarity in the series of proton compounds as well as in the series of complex ions is found in HI and  $ClO_4^-$ , which are relatively unstable substances. Attachment of a proton or cations of heavy metals, which disturb the symmetry of  $ClO_4^-$ , leads to explosive properties. This recalls the case of cupric halides in which the deformation of the halide ions by the  $Cu^{++}$  and consequent decrease in polarity increases from the fluoride to the bromide, and leads ultimately to the instability of  $CuI_2$ .<sup>17</sup>

The generalization of this relation furnishes an understanding of the instability or non-

<sup>16</sup> The contrary conclusion was reached by Pauling (see Introduction) because the S-O distance in  $SO_4^{2-}$  is not the sum of his single bond radii for S and O. As will be explained in a future paper this deviation from additivity is to be expected from the point of view of the polarization theory without the assumption of double bonds.

<sup>17</sup> K. Fajans, Naturwiss. **11**, 165 (1923).

existence of certain other compounds. Thus one would expect that the polarizability of the anion of the element 85 would be considerably higher than that of  $I^-$ . The discoverers<sup>18</sup> of the radioactive species of this element report that it does not co-precipitate with  $AgI$  and behaves like a metallic element rather than as a halogen. One can express this fact from the above point of view by saying that the large deformability expected for the anion of ekaiodine leads to the instability of its salts.

In  $CO_3^{=}$  the refraction per oxygen octet (4.08) is smaller than in the analogous  $SiO_3^{=}$  (4.42) because the field of the small  $C^{4+}$  (helium type) is stronger than that of  $Si^{4+}$  (neon type). Thus by analogy one would expect  $O^{=}$  in  $FO_4^-$ ,  $FO_3^+$ , or  $FO_2^{3+}$  to be deformed by the very small  $F^{7+}$  still more strongly than by  $Cl^{7+}$  in  $ClO_4^-$ . None of these complex ions of fluorine exists; however,  $F_2O$  is a stable compound,

<sup>18</sup> D. R. Corson, K. R. MacKenzie, and E. Segrè, *Phys. Rev.* **58**, 672 (1940).

which can be considered as formed by interaction within the grouping  $F-O^2+F^-$ . One can interpret the imaginary reaction  $2KFO_4 \rightarrow F_2O + K_2O + 3O_2$  as the result of the strong deformation of the oxygen ions by  $F^{7+}$ . Obviously this is only a way of formulating the fact that the electron affinity of fluorine is larger than that of oxygen. However, the advantage of the above point of view becomes evident when one tries to explain why  $ClO_4^-$  exists but  $BrO_4^-$  is unknown. The probable reason is that  $Br^{7+}$  has a non-rare gas structure and must have a much larger deforming power<sup>19</sup> than  $Cl^{7+}$ , as does  $Cu^+$  compared with  $Na^+$ . The ion  $I^{7+}$ , which also is of the non-rare gas type but which must be considerably larger than  $Br^{7+}$ , combines with  $O^{=}$  to form relatively stable periodates. From our point of view, this would mean that  $I^{7+}$  exerts a smaller influence on the oxygen octet than does  $Br^{7+}$ , for the same reason the  $Cl^{7+}$  has a smaller influence than has  $F^{7+}$ .

<sup>19</sup> K. Fajans, *J. Chem. Phys.* **9**, 281, 378 (1941).

## Polarization of Light Scattered by Isotropic Opalescent Media\*

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A general study is given of the polarization of light scattered by isotropic media whose elements of heterogeneity are not very small in comparison with the wave-length, (suspensions, colloidal solutions, solutions of large molecules, . . .). This includes an extension of a theory by R. S. Krishnan, who, considering certain particular states of polarization of the incident light and applying the law of reciprocity, had proved the equality of two of the four coefficients which are to be considered in these cases. Using Stokes' linear representation of the polarization of light beams, it is shown that the scattering through a given angle and for a given wave-length is characterized by the 16 coefficients of the linear forms which express the four polarization parameters of the scattered beam in terms of

the four corresponding parameters of the incident beam and that the law of reciprocity leads to six relations between these sixteen coefficients. For an isotropic asymmetrical medium (having rotatory power), the scattering is thus characterized by *ten* independent coefficients. In the case of a symmetrical medium, four of these coefficients must be zero, leaving only *six* scattering coefficients, and if the scattering particles are spherical, there are two additional relations between these coefficients. The comparison with dipolar scattering by very small elements shows that the best test to prove multipolar scattering is the existence of some ellipticity in the scattered light when the incident beam is linearly polarized in a direction oblique to the scattering plane.

### I

**T**HE scattering of light by a macroscopically homogeneous medium is caused by some

microscopical structure. If the dimensions of the elements of this structure are very small in comparison with the wave-length of the light, the scattering has the well-known simple characteristics of secondary dipolar emission.<sup>17-20</sup> But if

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