

structure. It is very difficult to prepare free from carbon or nitrogen. Uranium dioxide has the fluorite structure, $a = 5.4581 \text{ \AA}$. Oxygen is soluble in the fluorite structure up to approximately the composition $\text{UO}_{2.25}$ at which point the lattice constant is $a = 5.4297 \text{ \AA}$. U_2O_5 is orthorhombic,

$a = 8.27 \text{ \AA}$, $b = 31.65 \text{ \AA}$, $c = 6.72 \text{ \AA}$. The structure is related to those of U_3O_8 and UO_3 . A one phase region exists from U_2O_5 to UO_3 in which the various structures continuously transform from one to another.

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[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL CHEMISTRY, COUNCIL FOR SCIENTIFIC & INDUSTRIAL RESEARCH]

Basic Fluorides of Aluminum

BY J. M. COWLEY AND T. R. SCOTT

Introduction

The readiness with which aluminum and fluorine form complex ions in solution has been demonstrated by Brosset,¹ who determined the proportions of ions of the type AlF_n (where $n = 1$ to 6) in dilute solutions at constant activity. In solutions containing both aluminum fluoride and sulfate, the complex cations AlF_2^{2+} and AlF_2^+ appear to predominate, and the former may well be present in the salt $\text{AlF}_3 \cdot \text{Al}_2(\text{SO}_4)_3$ or $(\text{AlF})\text{SO}_4$, discovered by Ehret and Frere.² Various Russian workers, e.g., Nikolaev,³ have described the preparation of aluminum fluosulfate, $(\text{AlF}_2)_2\text{SO}_4$ or $4\text{AlF}_3 \cdot \text{Al}_2(\text{SO}_4)_3$, although Ehret and Frere found no evidence for the formation of this compound in the system $\text{AlF}_3\text{-Al}_2(\text{SO}_4)_3\text{-H}_2\text{O}$ at 25° . It is thus conceivable that aluminum might form hydroxy- (or oxy-) fluorides having the compositions $\text{AlF}(\text{OH})_2$ and $\text{AlF}_2(\text{OH})$: methods for the preparation of the latter compound (or the oxyfluoride $(\text{AlF}_2)_2\text{O}$) have indeed been given in several Russian patents.^{4,5} Apart from the work of Schober and Thilo,⁶ who described the diffraction pattern of $\text{Al}_7\text{O}_{10}\text{F}$ (prepared by the thermal hydrolysis of aluminum fluoride), no X-ray diffraction studies of these compounds have been made. The present paper describes the preparation of basic fluorides with compositions varying within the limits AlF_3 and $\text{Al}(\text{OH})_3$, and gives details of their crystallographic structures.

Experimental

The basic fluorides may be precipitated from solutions of aluminum fluosulfate by treatment with ammonia³ or by hydrolysis at temperatures ranging from $100\text{-}180^\circ$.⁴ Aluminum fluonitrate solution may also be neutralized with calcium carbonate, leaving calcium nitrate in solution and precipitating basic aluminum fluoride.⁵ Solutions of aluminum fluoride undergo slight hydrolysis on boiling, but the precipitate is very gelatinous and difficult to manipulate. While it is probable that hydrolysis at $150\text{-}200^\circ$ would produce basic fluorides in better yield and in more satisfactory physical form, suitable corrosion-resistant equipment for this method was not available.

(1) Brosset, "Electro-chemical and X-Ray Crystallographic Investigation of Complex Aluminum Fluorides," Stockholm, 1942.

(2) Ehret and Frere, *THIS JOURNAL*, **67**, 64 (1945).

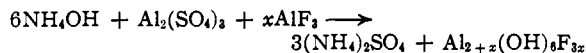
(3) Nikolaev, *J. Chem. Ind. U. S. S. R.*, **14**, 1087 (1937).

(4) Kashcheev and Lazarev, Russian Patent 46,256 (Mar. 31, 1936).

(5) Morozov and Ivanov, Russian Patent 53,812 (Sept. 30, 1938).

(6) Schober and Thilo, *Ber.*, **73B**, 1219 (1940).

For the present study, samples were prepared by the addition of ammonia to solutions of aluminum sulfate containing varied proportions of aluminum fluoride. The aluminum sulfate was of A.R. grade, while solutions of aluminum fluoride were prepared by dissolving Laboratory Reagent grade aluminum metal in A.R. hydrofluoric acid. The general reaction was



where x was varied from 0.4 to 14.0. Nikolaev³ used this method for the production of AlF_2OH and his directions for the use of 20% more than the theoretical quantity of ammonia and for subsequent boiling of the gelatinous suspension of basic fluoride were carefully followed. (With a greater excess of ammonia, the fluorine content of the basic fluoride is considerably reduced.) After boiling for two hours, the suspensions were filtered and the basic fluorides thoroughly washed with water. The products were dried at 130° , again washed with water to remove entrained ammonium sulfate, and dried for a further four to six hours at 130° . No sulfate could be detected in the final products, though in all instances combined ammonia was present. Attempts to prepare uncontaminated basic fluorides by other methods were no more successful. The compound obtained by hydrolysis of aluminum fluosulfate solution at 100° contained 5% of sulfate, and it is highly probable that the treatment of aluminum fluonitrate with calcium carbonate would also yield an impure product. A further sample was obtained by adding ammonia to molar aluminum fluoride solution until the pH reached 6.4, and consisted of a mixture of almost equal parts by weight of aluminum basic fluoride and ammonium tetrafluoroaluminate.

All specimens were analyzed for aluminum, fluorine, silica and ammonia, the oxygen content being calculated from the atomic ratio Al:F and the water content being obtained by difference. Aluminum was precipitated and weighed as the hydroxyquinolate, after fusion of the sample with potassium pyrosulfate or digestion with concentrated sulfuric acid. Fluorine was determined by the Willard-Winter distillation followed by titration of an aliquot of the distillate with thorium nitrate solution. Silica was estimated by a distillation method⁷ devised by one of the authors.

X-Ray diffraction patterns were obtained from all samples with the 14.3 cm. powder-camera of the General Electric XRD unit, using filtered cobalt $K\alpha$ radiation. The powder was packed into a wedge using a dilute solution of collodion in amyl acetate as binder and rocked through an angle of 20° during the exposure. To obtain the relative intensities of the lines, a key pattern, that from sample 4 (Table II), was microphotometered and used as an intensity standard. In the powder-wedge method, the reflections at small angles are weakened by absorption. The extent of this effect was estimated by comparison of the intensities of the key pattern with those given by a fine cylindrical sample, and the appropriate correction was made to the observed intensities of the diffraction lines.

(7) Scott, *J. Council Sci. Ind. Research (Australia)*, **19**, 103 (1946).

Results

Composition of Basic Fluorides.—Empirical formulas for the compounds prepared are given in Table I. It is interesting to compare the formula of sample 6 with the compound $\text{Al}_2\text{OF}_4 \cdot 3.5\text{H}_2\text{O}$ (*i. e.*, $\text{Al}(\text{OH})\text{F}_2 \cdot 1.25\text{H}_2\text{O}$) described by Kashchev and Lazarev.⁴ The samples contained silica (0.2–1.8%) and ammonium hexafluoroaluminate (2.3–7.3%) as impurities, but neither of these was found to produce lines in the X-ray powder photographs. With “amorphous” ammonium hexafluoroaluminate, it is quite possible that the diffuse lines caused by 7% of the material would not be apparent in the diffraction patterns.

TABLE I
COMPOSITION OF BASIC FLUORIDES

Sample no.	Al	Empirical formula ^a		H ₂ O	Percentage of ammonium hexafluoroaluminate
		OH	F		
1	1	2.60	0.40	0.25	2.3
2	1	2.30	.70	.31	4.1
3	1	1.98	1.02	.58	7.0
4	1	1.35	1.65	1.09	6.0
5	1	1.25	1.75	1.14	7.2
6	1	1.04	1.96	0.90	7.3
7	1	0.93	2.07	0.91	4.4

^a Corrected for presence of $(\text{NH}_4)_2\text{AlF}_6$.

Ammonium hexafluoroaluminate was distinguished by the fact that at 300°, in air, it decomposes almost completely to aluminum fluoride and volatile ammonium fluoride. By contrast, ammonium tetrafluoroaluminate is relatively stable and retains the greater part of its ammonia until higher temperatures are reached. The latter compound was identified by its diffraction pattern in the precipitate obtained by the treatment of aluminum fluoride solution with ammonia, but was only present in minor quantities, if at all, in the samples listed in Table I. It is noteworthy that the ammonium hexafluoroaluminate inferred to be present could not be removed from the basic fluorides by leaching with water, despite its appreciable solubility (0.76 at 25°). Nevertheless, the ignition behavior of the contaminated oxyfluorides, with respect to their ammonia contents, was so closely parallel to that of ammonium hexafluoroaluminate, that no doubt is felt as to the presence of the latter compound.

Although only a small excess of ammonia was used in the preparation of the basic fluorides, a portion of the fluorine was lost by reactions of the type $\text{NH}_4\text{OH} + \text{AlF}_2\text{OH} \rightarrow \text{NH}_4\text{F} + \text{AlF}(\text{OH})_2$. When the atomic ratio F:Al did not exceed 2:1 in the solutions used, the ratio in the resulting basic fluorides was, on the average, about 10% smaller, but increase of the ratio beyond 2:1 did not result in a proportional increase in the basic fluoride obtained. Sample 7, for example, with a F:Al ratio of 2.07:1, was prepared from solution of aluminum sulfate and fluoride in which the ratio was 2.63:1, and the former ratio was not ex-

ceeded even in basic fluorides prepared from aluminum fluoride solutions alone.

X-Ray Diffraction Studies.—Except for sample 1, all samples gave the same line-pattern, and in no case were any lines due to aluminum oxides, fluorides or any other impurities observed. Sample 1 gave only diffuse haloes such as are obtained from “amorphous” aluminum hydroxide. These diffuse haloes were present faintly with the line-patterns from 2 and 3. Samples 4 and 5 gave good patterns of sharp lines. For 6 and 7 the lines were broadened, indicating smaller crystal size.

The pattern from no. 4 was measured and analyzed in detail. The lattice spacings and intensities are set out in Table II. Spacings agree with those for a cubic structure with unit cell dimension $a_0 = 9.829 \pm 0.010 \text{ \AA}$. The missing reflections indicate the space group $\text{O}_h^7 - \text{Fd}3m$.

TABLE II
LATTICE PLANE SPACINGS AND INTENSITIES FROM HYDROXYFLUORIDE PATTERNS

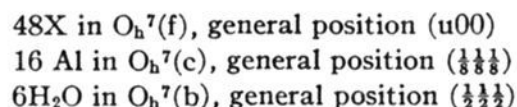
Reflection	Dried at 130° ^a				Dehydrated at 500° ^b	
	<i>d</i> _{obs.}	<i>d</i> _{calcd.}	Int. _{obs.}	Int. _{calcd.}	Int. _{obs.}	Int. _{calcd.}
111	5.70	5.67	460	490	680	750
220	...	3.48	31	27
311	2.979	2.964	220	203	105	113
222	2.841	2.837	100	100	100	100
400	2.460	2.457	26	20	9	7
331	2.258	2.255	21	20	8	5
422	2.009	2.006	44	46	74	86
333	1.893	1.892	92	106	80	93
511						
440	1.737	1.737	110	110	71	85
531	1.661	1.661	33	30	37	51
620	1.553	1.554	26	26	17	14
533	1.498	1.499	40	42	26	31
622	1.480	1.482	42	42	32	42
444	1.417	1.418	9	8	7	12
711	1.375	1.376	51	44	41	70
551						
731	1.277	1.279	45	58	30	42
553						
800	1.227	1.228	13	17		
733	1.201	1.201	2	3		
822	1.158	1.158	31	28		
660						
662	1.127	1.127	17	22		
840	1.099	1.099	14	15		
911	1.079	1.079	10	8		
753						
664	1.047	1.048	9	14		
931	1.031	1.030	20	37		

^a Sample 4, containing 6 molecules of water per unit cell.

^b Sample 6, containing no molecules of water per unit cell after dehydration.

The measured density is 2.25. Assuming that only one third of the water is in the lattice, this gives 16 $\text{AlX}_3 \cdot 6\text{H}_2\text{O}$ per unit cell, where X may be (OH) or F. (The remaining water is less firmly held and is apparently absorbed physically.)

This group may be fitted into the unit cell as follows



the six molecules of water being distributed among the eight sites.

Agreement between calculated and observed intensities is obtained for $u = 3/16$. With this value of u , the hydroxyl and fluorine ions lie at the corners of regular octahedra with aluminum ions arranged tetrahedrally, as centers, and form part of a hexagonal close-packed lattice. Each hydroxyl or fluorine ion is shared by two octahedra. The water molecules lie at the mid-points of the edges, at the body center, and at the centers of the unfilled segments of the unit cube (Fig. 1). This arrangement gives the distances between neighboring atoms as

Al—F, O _{OH}	1.84 Å.
F, O _{OH} —F, O _{OH}	2.61 Å.
F, O _{OH} —O _{H₂O}	3.07 Å.

These values are consistent with those for similar groups in other compounds. The observed intensities and those calculated for this structure are compared in Table II. Intensities calculated for more or less than six molecules of water in the lattice give less satisfactory agreement. The intensity of the 222 line does not vary with the number of water molecules present, and has been taken as the standard for the comparison of intensities.

The line patterns from the other samples had the same relative intensities, but the unit cell dimension was found to vary. Corresponding to the progressive replacement of hydroxyl by fluorine ions, which have smaller ionic radius, the lattice constant decreased regularly with increasing fluorine content as shown in Table III.

TABLE III

VARIATION OF LATTICE CONSTANT WITH FLUORINE CONTENT

Sample	Ratio F:Al	Lattice constant	
1	0.40	..	Diffuse haloes only
2	0.70	9.85	Diffuse haloes present
3	1.02	9.84	Diffuse haloes present
4	1.65	9.83	
5	1.75	9.81	
6	1.96	9.77	Lines broader
7	2.07	9.77	Lines broader

Effect of Ignition on Basic Fluorides.—Samples were weighed into platinum crucibles and heated for three hours in an electric furnace at temperatures ranging from 200 to 600°. Material ignited at 300° or more was gritty and hygroscopic, sample 6 regaining more than half the weight lost at 300°, when exposed to the air for three days. The hygroscopicity was less marked in samples ignited at 500–600°.

At 600°, the basic fluoride pattern of sample 6

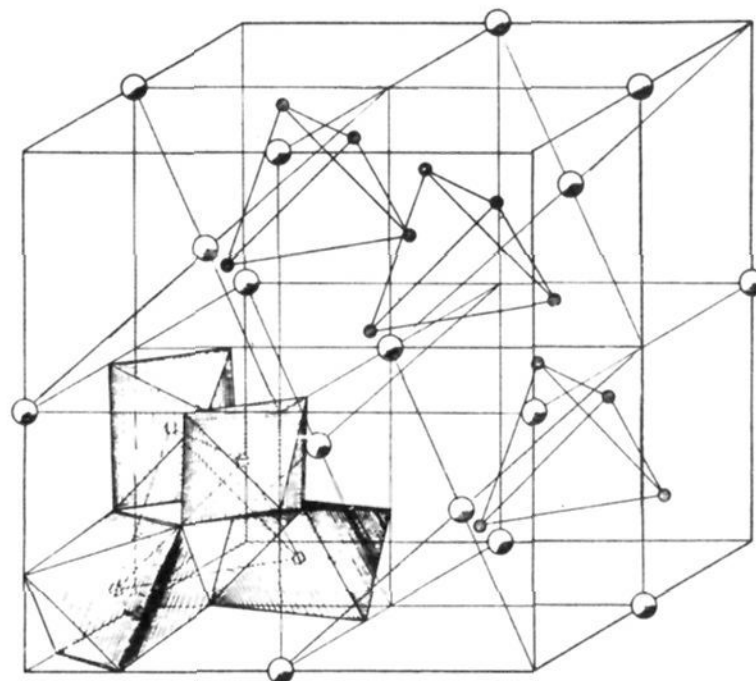


Fig. 1.—Unit cell of aluminum hydroxyfluoride containing 16 Al(F,OH)₃·6H₂O: ●, aluminum; ○, water (only 6 of the 8 sites per unit cell shown are occupied by water molecules); fluorine or hydroxyl ions occupy the corners of the octahedra surrounding the aluminium ions, as shown in only one octant of the unit cube.

was replaced by lines due to fluorides and oxides of aluminum. Ignition at 300, 400 and 500° gave basic fluoride patterns showing a progressive decrease in lattice constant (Table IV) and a progressive variation in relative intensities of the lines. In particular the 220 line became visible and increased in intensity. The observed intensity variations follow closely those of the intensities calculated for the removal of the six water molecules from the lattice. The observed intensities for sample 6 heated to 500° are compared in Table II with those calculated for a structure in which no water molecules remain. The number of molecules of water remaining, corresponding to the intensity distribution at each stage of the heating, is given in the third column of Table IV.

TABLE IV

PROPERTIES OF IGNITED BASIC FLUORIDES

Sample	Lattice constant	Molecules of water/unit cell	Ignition loss	
			Calcd., %	Actual %
3 unheated	9.84	6		
3 heated 400°	9.65	0	14.7	28.9
6 unheated	9.77	6		
6 heated 300°	9.72	5	14.6	19.6
6 heated 400°	9.65	2	18.0	23.7
6 heated 500°	9.63	0	20.2	25.5

Discussion

In the introductory remarks, it was stated that aluminum might form either the hydroxyfluorides AlF(OH)₂ and AlF₂(OH), or the corresponding oxyfluorides AlFO and (AlF₂)₂O, when solutions containing the complex cations AlF⁺⁺ and AlF₂⁺ were treated with ammonia. X-Ray diffraction

studies support this view, but the ionic radii of fluorine and hydroxyl ions are so similar that the same crystal structure serves for the range of composition from $\text{AlF}(\text{OH})_2$ to AlF_2OH . The small decrease in lattice constant, as the proportion of fluorine increases, is not only incompatible with an oxyfluoride structure but also shows that the samples do not merely consist of mixtures of aluminum hydroxide or fluoride with a single hydroxyfluoride of constant composition. Assuming that the ionic radii of the oxygen and fluorine ions in the hydroxyfluoride structure are in the same ratio as those given by Pauling⁸ for a sodium chloride-type structure, the decrease in unit cell dimension is calculated as 0.7% for a change in composition from $\text{AlF}(\text{OH})_2$ to $\text{AlF}_2(\text{OH})$. The observed decrease of 0.8% is in good agreement with this figure. (The ionic radius of hydroxyl ion is only slightly greater than that of oxygen ion.⁹)

It is improbable that cations containing more fluorine than AlF_2^+ , or less than AlF^{++} , exist in solution to any important extent, and the range of hydroxyfluoride compositions is consequently confined to the limits given above. Despite numerous attempts to prepare samples with a F:Al ratio significantly greater than 2:1, the highest value obtained was 2.07:1 (sample 7) and this is almost certainly due to the presence of small quantities of aluminum fluoride. Samples 1 and 2 contain a smaller proportion of fluorine than $\text{AlF}(\text{OH})_2$, but are contaminated with considerable amounts of aluminum hydroxide, the presence of which is revealed not only by the X-ray diffraction data (Table III) but also by the much smaller water content of these samples when compared with purer basic fluorides (nos. 4-7).

Dehydration of the hydroxyfluorides might be expected to yield oxyfluorides which would obviously differ in structure with variation in their fluorine content. Samples 3 and 6 were chosen for investigation because simple dehydration would produce AlFO and $(\text{AlF}_2)_2\text{O}$, respectively, but, even at 500°, the hydroxyfluoride structure was retained. At higher temperatures, decomposition to aluminum fluoride and oxide occurred and no evidence was obtained for the formation of distinct oxyfluoride structures. It is of interest to note that fluorine may be completely removed from ignited hydroxyfluorides by the Willard-Winter distillation, using 55% sulfuric acid, but that, once decomposition has occurred, only a small fraction of the fluorine can be released by this method.

The loss of weight of hydroxyfluorides was found to increase smoothly with temperature up to 500° and no distinction could be made between loss of loosely-combined water, crystal water (*i. e.*, 6 moles per unit cell) and water derived from the conversion of hydroxyl to oxygen ions. The

(8) Pauling, *THIS JOURNAL*, **49**, 765 (1927).

(9) W. H. and W. L. Bragg, "The Crystalline State," G. Bell and Sons, London, 1933, p. 122.

latter process might be expected to result in the formation of oxyfluorides, but the hydroxyfluoride structure was retained in sample 3 when slightly more than 50% of the hydroxyl groups were thus decomposed. Table IV shows the actual ignition losses at various temperatures, compared with the losses calculated on the basis that hydroxyl ions were undisturbed and that crystal water was lost in amounts determined from the change in intensities of the lines of the diffraction patterns. It is evident that conversion of hydroxyl to oxygen ions must occur simultaneously with loss of crystal water at all temperatures from 300-500°. This would not have any great effect upon the X-ray line intensities.

Two factors combine to increase the calculated ignition losses given in Table IV. As with most hydrated fluorides, thermal hydrolysis occurs during ignition, resulting in loss of hydrogen fluoride instead of water, but it is unlikely that more than 10% of the fluorine is lost in this fashion, even at 500°. The corresponding increase in the calculated ignition loss is 1 to 2%. The second factor depends on the presence of aluminum hydroxide in samples 1, 2 and 3, as demonstrated by the diffraction patterns. Assuming that this contaminant is present to the extent of 25% and decomposes to $\gamma\text{-Al}_2\text{O}_3$ at 400°, the calculated ignition loss of sample 3 would be increased by a further 8%. Consideration of these two factors makes it possible to substitute a figure of 24% for that of 14.7% for the calculated ignition loss of sample 3 at 400° as given in Table IV. This brings the behavior of sample 3 more into line with that of sample 6, but still requires the destruction of at least 50% of the hydroxyl groups.

In the hydroxyfluoride structure derived above it was shown that the hydroxyl or fluorine ions formed regular octahedra about the aluminum ions. In both the fluoride and hydroxide there is a similar arrangement of ions except that the octahedra in these two cases are distorted. It may be concluded that the value of the radius of the negative ion which allows the six negative ions to surround the aluminum ion so that they just touch each other, lies between the values for the hydroxyl and fluorine ions. Thus groups of four hydroxyl and two fluorine, or two hydroxyl and four fluorine could be fitted about aluminum ions to give very nearly regular octahedra, whereas groups of either six fluorine or six hydroxyl would lead to deformation of the octahedra.

From the Al-F distance of 1.84 Å., the ionic radii are found to be 0.54 Å. for Al^{3+} and 1.30 Å. for the negative ions. This value for Al^{3+} lies between the values 0.57 Å., given by Goldschmidt,¹⁰ and 0.50 Å., given by Pauling,⁸ for coordination number 6. For oxygen and fluorine ions with the same coordination number, Goldschmidt gave 1.32 and 1.33 Å., and Pauling 1.40 and 1.36 Å., respectively, for the ionic radii.

(10) Goldschmidt, *Trans. Faraday Soc.*, **25**, 253 (1929).

The above value for the negative ions is lower than these, as would be expected from the lower value of the coordination number occurring in this structure.

Conclusions

The treatment of mixed solutions of aluminum fluoride and sulfate with ammonia produces hydroxyfluorides falling within the range of composition $\text{AlF}(\text{OH})_2$ to $\text{AlF}_2(\text{OH})$. These compounds are cubic with space group $\text{O}_h^7 - \text{Fd}3m$. The lattice constant decreases with increasing fluorine content from 9.85 to 9.77 Å. The unit cell con-

tains sixteen formula-groups plus six water molecules.

The hydroxyfluoride structure is stable up to 500°, the gradual loss of water being reflected by a corresponding contraction of the lattice. The remarkable stability of the lattice is demonstrated by the retention of the structure despite the destruction of more than half the hydroxyl groups at high temperatures. At 600°, the hydroxyfluoride structure is no longer evident. No oxyfluorides are formed, the hydroxyfluorides decomposing directly to aluminum oxide and fluoride.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Aqueous Ionization Constants of Inorganic Oxygen Acids

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It is presumably possible to determine independently the formulas, structures and aqueous ionization constants of inorganic acids. The data so obtained may then be correlated either empirically or on the basis of theories of molecular structure and of the process of ionization in solution, in which case the results of the comparison may serve as a test of the theories. A remarkably successful correlation has been obtained by Kossiakoff and Harker, in a paper on "The Calculation of Ionization Constants of Inorganic Oxygen Acids from their Structures,"¹ and the results have been interpreted as supporting the mechanism proposed as the basis of the calculation.² The purpose of this paper is to examine critically the treatment and results of Kossiakoff and Harker, and to determine which of their assumptions are supported by their calculations.

Kossiakoff and Harker assume (1) that the ionization constant of an oxygen acid is defined by the free energy of transfer of a proton from a hydroxyl group to the surrounding water structure, and (2) that this energy, in electrostatic terms, depends on (a) the formal charge of the central atom of the acid, (b) the number of non-hydroxyl oxygen atoms in the acid ion available for attachment of a proton, (c) the number of equivalent hydrogens available for "dissociation," and (d) the structure of the acid as determined by crystallographic data on its salts.³

We shall see that the first and main assumption is not effectively tested by the treatment of Kossiakoff and Harker, and that the test of 2(c)

(1) A. Kossiakoff and D. Harker, *THIS JOURNAL*, **60**, 2047 (1938).

(2) For a discussion of their method and results, see O. K. Rice, "Electronic Structure and Chemical Binding," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 429-438.

(3) "Structure" refers not to the formula but to the physical quantities of bond angles and interatomic distances. A formula such as $\text{Ge}(\text{OH})_4$, graphical or otherwise, is the result of chemical and analytical reasoning, independent of the physical determination of the structure of the substance.

and 2(d) is entirely inconclusive, but that the assumptions 2(a) and 2(b) are effective and lead to very enlightening empirical correlations.

I. Calculations of Kossiakoff and Harker

The general expression used by Kossiakoff and Harker for the free energy change fixing a particular ionization constant is

$$\Delta F = \sum W_i - C + RT \ln n_o/n_H \quad (1)$$

Here C is a solvent constant, n_o is the number of equivalent non-hydroxyl oxygens in the ion being formed, n_H is the number of equivalent (transferable) hydrogens in the acid, and W_i is the electrostatic energy of a single transfer. Furthermore

$$W_i = \sum_j \frac{m_j e}{\epsilon} \left(\frac{1}{r_j} - \frac{1}{r_j'} \right) \quad (2)$$

in which $r_j' - r_j$ is the displacement of the proton relative to the j 'th atom of the solute particle, whose formal charge is m_j ; e is the charge of the electron and ϵ the dielectric constant of the medium. The formal charge of an atom is its group number in the periodic table minus the number of electrons in its valence shell, a shared pair being counted as one.

For the evaluation of C , Kossiakoff and Harker chose K_1 of orthophosphoric acid H_3PO_4 ($pK_1 = 2.1$, $\Delta F = 2.9$) as reference; from structural data they calculated $\sum W_i = 46.1$. For this calculation, the first term of $\sum W_i$, or the term for the first transfer, from hydroxyl to adjacent water molecule, was taken as

$$W_1 = \frac{e^2}{\epsilon} \left[\left(\frac{1}{R} - \frac{1}{R'} \right) - \left(\frac{1}{\rho} - \frac{1}{\rho'} \right) + \left(\frac{1}{d} - \frac{1}{d'} \right) \right] \quad (3)$$

in which $R' - R$ is the absolute displacement of the proton (R being the original O—H distance), $\rho' - \rho$ its displacement relative to the central atom, phosphorus (with $m = +1$), and $d' - d$ its displace-