| TABLE I |  |
|---------|--|
|---------|--|

The Ionization Constants of  $\beta$ -Alanine in 0, 5, 10 and 20% Isopropyl Alcohol

| Alcohol,<br>% | 0°   | 5°   | 15°                     | 25°  | 35°  | 40°  |
|---------------|------|------|-------------------------|------|------|------|
|               |      | Ĺ    | $K_A \times 10^4$       | i    |      |      |
| 0             | 2.21 | 2.36 | 2.61                    | 2.81 | 2.99 | 3.04 |
| 5             | 1.93 | 2.08 | 2.33                    | 2.52 | 2.69 | 2.73 |
| 10            | 1.69 | 1.83 | 2.07                    | 2.28 | 2.42 | 2.48 |
| 20            | 1.32 | 1.46 | 1.70                    | 1.89 | 2.03 | 2.07 |
|               |      |      | $K_{\rm B} \times 10^4$ | ł    |      |      |
| 0             | 1.14 | 1.25 | 1.51                    | 1.73 | 1.92 | 2.02 |

From these equations the standard thermo-dynamic quantities  $\Delta F_i^0$ ,  $\Delta H_i^0$ ,  $\Delta C p_i^0$  and  $\Delta S_i^0$ for the ionization reactions may be calculated.<sup>3</sup>

Effect of Solvent.—Graphs of  $-\log K_A$  versus the mole fraction isopropyl alcohol and versus the reciprocal of the dielectric constant consist of families of smooth curves with greater curvature

# TABLE II Constants of the Equation - Log K = A/T + CT - D

|               | -       |                    |         |
|---------------|---------|--------------------|---------|
| Alcohol,<br>% | A       | С                  | D       |
|               | -       | - $\log K_{\rm A}$ |         |
| 0             | 1231.71 | 0.010957           | 3.8478  |
| 5             | 1594.69 | .014887            | 6.1904  |
| 10            | 1753.58 | .016375            | 7.1209  |
| 20            | 2351.54 | .022608            | 10.9051 |
|               | -       | - log Кв           |         |
| 0             | 1881.78 | 015784             | 7.2558  |

than those for propionic<sup>2</sup> and n-butyric<sup>3</sup> acids in the same solvents.

Acknowledgment.—The authors wish to express thanks to the Research Institute of The University of Texas for the financial aid, Project 205, which supported a part of this work, and to the Magnolia Petroleum Company for a fellowship which made possible its continuation.

AUSTIN, TEXAS

RECEIVED JULY 24, 1950

### [CONTRIBUTION FROM THE LABORATORY OF C. A. WAMSER]

# Equilibria in the System Boron Trifluoride–Water at $25^{\circ}$

## By Christian A. Wamser

The system  $BF_4-H_2O$  is investigated from dilute solutions to the dihydrate,  $BF_4\cdot 2H_2O$ . Evidence of the formation and hydrolysis of  $HBF_4OH$  in the reaction of  $BF_3$  with  $H_2O$  is afforded by conductance measurements, and suggests a mechanism by: k (in liters mole<sup>-1</sup> min.<sup>-1</sup>) = 0.064 + 7.35[H<sup>·</sup>] at 25°. The hydrolysis constant of HBF<sub>3</sub>OH, evaluated from kinetic considerations, is 0.011 at 25°. Mixtures of BF<sub>3</sub>-H<sub>2</sub>O at equilibrium contain the species: HBF<sub>4</sub>, HBF<sub>3</sub>OH, HBF<sub>2</sub>(OH)<sub>2</sub>, HBF(OH)<sub>3</sub>(?) and B(OH)<sub>3</sub>. Determination of the equilibrium composition from dilute solutions to the dihydrate is made strengths of the fluoboric acids are estimated from conductance data.

It has long been known that fluoboric and boric acids are produced when boron trifluoride reacts with water

$$4BF_3 + 3H_2O = 3HBF_4 + B(OH)_3$$

In an attempt to interpret the titratable acidities of aqueous solutions of boron trifluoride, and to account for the presence of fluoride ion at the titration end-point, Gasselin<sup>1</sup> has expressed the reaction as

$$2BF_{1} + 3H_{2}O \longrightarrow HBF_{4} + B(OH)_{3} + 2HF$$

However, both of the above equations have always been recognized as oversimplifications, since aqueous solutions of boron trifluoride do not contain the fluoride ions of hydrofluoric acid but behave as if an easily hydrolyzed form of fluoboric acid were present.<sup>2</sup>

No studies of kinetics or equilibria in the system boron trifluoride-water are reported in the literature,<sup>3</sup> and only recent investigations<sup>4,5,6</sup> have suggested the nature of the species that may be pres-

 V. Gasselin, Bull. soc. chim., [3] 7, 754 (1892).
 C. F. Swinehart, A. R. Bumblis and H. F. Flisik, Anal. Chem., 19, 28 (1947).

(3) H. S. Booth and D. R. Martin, "Boron Trifluoride and its Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1949.

(4) C. A. Wamser, THIS JOURNAL, 70, 1209 (1948).

(5) I. G. Ryss, Compt. rend. acad. sci. U. R. S. S., 52, 417 (1946).

(6) I. G. Ryss and M. M. Slutskaya, J. Phys. Chem. (U. S. S. R.), 21, 549 (1947).

ent and the analytical methods that might be applicable.

Nature of the Present Investigation.-The present investigation is concerned with the system boron trifluoride-water over the concentration range extending from dilute solutions to the dihydrate, BF<sub>3</sub>·2H<sub>2</sub>O. The range of stability of the dihydrate, generally conceded to exist as the pure compound H<sub>3</sub>O+BF<sub>3</sub>OH- at or below its melting point, is extended to 25° on the basis of conductance and analytical data. Evidence of the formation and hydrolysis of HBF3OH when BF3 reacts with water is afforded by conductance measurements, and suggests a mechanism for the experimentally observed (slow) formation of HBF4 on the basis of the reaction  $HBF_3OH + HF \rightarrow HBF_4$ + H<sub>2</sub>O. Determination of the equilibrium composition of  $BF_3$ - $H_2O$  mixtures is made possible by application of specially developed analytical techniques and methods. Electrometric titration of a solution of  $BF_8$ -H<sub>2</sub>O at equilibrium confirms the analytical interpretation of the relative concentrations of the various species. The hydrolysis constant of HBF<sub>3</sub>OH cannot be evaluated from analytical or conductance data and is hence approached from kinetic considerations. Finally, certain conclusions dependent upon this hydrolysis constant, such as the relative strengths of the fluoboric acids and their concentrations, are considered.

# Experimental

Boron trifluoride was prepared and purified by a standard procedure.<sup>7</sup> Boron trifluoride monohydrate and dihydrate were prepared as described by McGrath, Stack and McCusker.<sup>8</sup> Dihydroxyfluoboric acid was prepared from boron trifluoride and boric acid, and distilled as described by Sowa, Kroeger and Nieuwland.<sup>9</sup>

It was established that mixtures of  $BF_3$  (or the mono- or dihydrate) + H<sub>2</sub>O, or  $B(OH)_3$  + 3HF + H<sub>2</sub>O, or  $HBF_2(OH)_2$  + HF + H<sub>2</sub>O were identical, at equilibrium, for equivalent stoichiometric concentrations of  $BF_3$ .

It was found convenient to prepare the mixtures for establishment of equilibrium composition from boron trifluoride dihydrate and water, since the concentration range from very dilute aqueous solutions to the dihydrate was covered. For kinetic studies, the preparation from aqueous boric acid and aqueous hydrofluoric acid (in the mole ratio 1 to 3) is more convenient for reasons that will be indicated later.

In the experimental investigations to be discussed, solutions were prepared in polystyrene or polyethylene vessels, dilutions to definite volume were carried out in calibrated polystyrene volumetric flasks, aliquots were transferred by means of calibrated wax-lined pipets, and conductances were measured in specially constructed polystyrene cells.

measured in specially constructed polystyrene cells. The Hydrolysis of HBF<sub>3</sub>OH; Mechanism of the Reaction of BF<sub>3</sub> and  $H_2O$ .—When BF<sub>3</sub> reacts with water, the acid HBF<sub>3</sub>OH is first formed

$$3F_3 + H_2O \longrightarrow HBF_3OH$$
 (1)

Experimental evidence for this is afforded by the observation that the solution immediately after preparation is identical to one prepared by passing an aqueous solution of pure KBF<sub>3</sub>OH<sup>4</sup> through a column of the hydrogen form of a cation exchange resin such as Amberlite IR-100H.



Fig. 1.—Specific conductance (O) and pH ( $\bullet$ ) at 25°, measured immediately after prepr., of 0.0561 *M* boric acid treated with hydrofluoric acid.

HBF<sub>3</sub>OH is also immediately formed when one mole of boric acid (aqueous) is mixed with three moles of hydrofluoric acid (aqueous). This may be demonstrated by measurement, immediately after preparation, of the conductance and pH of a series of solutions each containing a fixed concentration of boric acid but increasing concentrations of hydrofluoric acid. The addition of HF to B(OH)<sub>3</sub> causes a sharp increase in conductance and a corresponding decrease in pH (Fig. 1) up to F/B = 3. Beyond this point the conductance increases (and the pH decreases) only very slowly (HF is a much weaker acid than HBF<sub>3</sub>OH). The reaction is

$$(OH)_3 + 3HF \longrightarrow HBF_3OH + 2H_2O$$
 (2)

The conductance of the solution at  $HF/B(OH)_3$ = 3 (*i.e.*, point B) is appreciably lower than that corresponding to the intersection of the extrapolated conductance lines (*i.e.*, point A). This latter may be regarded as representing the conductance of the acid HBF<sub>3</sub>OH free from its hydrolysis products, and the actual measured value as representing the conductance of HBF<sub>3</sub>OH in equilibrium with its hydrolysis products. By analogy to the hydrolysis of HBF<sub>4</sub>,<sup>4,5</sup> the hydrolysis of HBF<sub>3</sub>OH probably proceeds as indicated by

$$BF_{3}OH + H_{2}O \longrightarrow HBF_{2}(OH)_{2} + HF \quad (3)$$

The assumption that this hydrolytic equilibrium is very rapidly established (in contrast to the slow hydrolysis of HBF<sub>4</sub>) is further supported by the following experimental evidence: (a) Titrations of aqueous solutions of pure KBF<sub>4</sub> and pure KBF<sub>3</sub>OH with thorium nitrate in the presence of alizarin red S, indicate that none of the fluorine in BF<sub>4</sub>- is available, but the fluorine in BF<sub>3</sub>OH<sup>-</sup> is rapidly and quantitatively available. (b) Aqueous solutions of pure KBF<sub>4</sub> are only very slowly hydrolyzed by alkali; in contrast, a solution of KBF<sub>3</sub>OH may be rapidly and quantitatively hydrolyzed to fluoride and metaborate ions under the same conditions.

A small fraction of the concentration of  $HBF_2$ -(OH)<sub>2</sub> represented as in equilibrium in (3), is probably also hydrolyzed to  $HBF(OH)_3$ , a small fraction of which is, in turn, in equilibrium with boric acid

$$HBF_{2}(OH)_{2} + H_{2}O \swarrow HBF(OH)_{3} + HF \quad (3a)$$
$$HBF(OH)_{3} \swarrow B(OH)_{3} + HF \quad (3b)$$

(The analytical behavior of aqueous solutions of  $KBF_2(OH)_2$  and  $KBF_3OH$  is identical with respect to fluorine lability.)

Equations (1) and (3) then represent the first two stages of the reaction of boron trifluoride and water. Reaction (1) is immeasurably fast and the equilibrium expressed by reaction (3) is also very rapidly established. The solution at this stage does not contain any HBF<sub>4</sub> (nitron test), but on standing, HBF<sub>4</sub> is slowly formed, according to the reaction

$$HBF_3OH + HF \longrightarrow HBF_4 + H_2O$$
 (4)

This reaction is slow and its kinetics have already been investigated<sup>4</sup> for the special case  $[HBF_3OH] = [HF]$  (second order). In the present case, however, as the reaction proceeds, the HF for reaction (4) is supplied from the hydrolysis of the acids HBF<sub>3</sub>OH, HBF<sub>2</sub>(OH)<sub>2</sub> and HBF(OH)<sub>3</sub>.

<sup>(7)</sup> H. S. Booth, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., New York, N. Y., 1939, p. 21.

<sup>(8)</sup> J. S. McGrath, G. G. Stack and P. A. McCusker, This JOURNAL, 66, 1263 (1944).

<sup>(9)</sup> F. J. Sowa, J. W. Kroeger and J. A. Nieuwland, *ibid.*, **57**, 454 (1935).

The final solution, at equilibrium, can accordingly contain the following species: HBF<sub>4</sub>, HBF<sub>3</sub>-OH, HBF<sub>2</sub>(OH)<sub>2</sub>, HBF(OH)<sub>3</sub> and B(OH)<sub>3</sub>. Only the acid HBF(OH)<sub>3</sub> has never been isolated.<sup>3</sup>

Special Analytical Methods.—The species that may be present have been indicated above. In some of the equilibrium mixtures (at 25°), part of the boric acid is present as a solid phase.

The following analytical methods were developed for establishment of the equilibrium composition of species in the system  $BF_4-H_2O$ :

the system  $BF_{4}-H_{2}O$ : (1) HBF<sub>4</sub>.—Of the various species that may be present, only HBF<sub>4</sub> is precipitated by the base "nitron." An aliquot of the solution is pipetted into an excess of ice-cold nitron acetate, the precipitated  $C_{20}H_{16}N_4$ ·HBF<sub>4</sub> separated by centrifugation or filtration, washed with ice-water (previously saturated with nitron fluoborate), and dissolved in acetone. The acetone solution is diluted with four volumes of water, one volume of chloroform is added, and the HBF<sub>4</sub> is titrated with standard alkali hydroxide to the phenolphthalein end-point, the mixture being vigorously agitated during the titration. As the HBF<sub>4</sub> is neutralized, the libcrated nitron, which is insoluble in water, transfers completely into the chloroform phase.

pletely into the chloroform phase. (2) HBF<sub>3</sub>OH (+HBF<sub>2</sub>(OH)<sub>2</sub> + HBF(OH)<sub>3</sub>).—The acids of the hydroxyfluoboric acid group cannot be distinguished from one another by analytical methods and may conveniently be determined as a group and expressed as HBF<sub>3</sub>OH. (However, it will be indicated later that the relative concentrations of HBF<sub>3</sub>OH and HBF<sub>2</sub>(OH)<sub>2</sub> may be estimated from equilibrium constants.)

The hydroxyfluoboric acids may be determined by either of two methods:

(a) Unlike  $BF_4^-$ , the hydroxyfluoborate ions are readily amenable to hydrolysis by alkali hydroxide, fluoride and metaborate ions being produced. An aliquot of the solution is treated with an excess of calcium chloride, and titrated to the methyl orange end-point, using standard alkali hydroxide

 $HBF_4 + NaOH \longrightarrow NaBF_4 + H_2O$ 

 $2HBF_{3}OH + 3CaCl_{2} + 6NaOH \longrightarrow$ 

C

$$3CaF_{2} + 6NaCl + 2B(OH)_{3} + 2H_{2}O$$
$$HBF_{2}(OH)_{2} + CaCl_{2} + 2NaOH \longrightarrow$$

 $CaF_2 + 2NaCl + B(OH)_1 + H_2O$ 2HBF(OH)\_1 + CaCl\_2 + 2NaOH  $\longrightarrow$ 

$$aF_2 + 2NaCl + 2B(OH)_1 + 2H_2O$$

If the concentration of  $HBF_4$  has been determined as in (1), the titration equivalent to the hydroxyfluoboric acids may be obtained by difference.

(b) The hydroxyfluoborate ions bleach the thorium alizarin red S lake in dilute acid medium, while  $BF_4^-$  has no action: An aliquot of the solution is appropriately diluted, treated with alizarin red S, and titrated with standard thorium nitrate solution as in the standard procedure for fluorine.

(3)  $B(OH)_{2}$  (Soluble).—The solution which has been adjusted to the methyl orange end-point, in the presence of calcium chloride, is then treated with mannitol and titrated further with alkali hydroxide to the phenolphthalein endpoint. One-third of the titration equivalent to  $HBF_{3}OH$  (from (2)) is deducted (to correct for the boric acid resulting from the decomposition of the hydroxyfluoborates), and the net volume of standard alkali used to calculate  $B(OH)_{3}$ . (4)  $B(OH)_{3}$  (Insoluble).—In those cases in which part

(4)  $B(OH)_3$  (Insoluble).—In those cases in which part of the boric acid is present as a solid phase in the equilibrium mixture, a measured volume of the well-mixed slurry is filtered at 25°, and aliquots of the filtrate taken for determinations (1), (2) and (3). The boric acid on the filter is washed with ice-water which has been saturated with boric acid, and is then dissolved in water and titrated in the usual manner. The weight of the (solid) boric acid thus determined is then also used to calculate its volume in the original equilibrium slurry, and the value of the filtrate aliquots accordingly estimated in terms of the original slurry.

(5) Total Boron or Fluorine.—In those cases for which total boron or total fluorine was determined, the methods of Ryss<sup>10,11</sup> were employed. (Boron is determined by boiling

the solution of the sample under reflux, in the presence of an excess of calcium chloride, until no further acid titratable to methyl orange is liberated. The boric acid is titrated in the presence of mannitol. Fluorine is determined by boiling the solution of the sample with potassium chlorate and iodide in the presence of an excess of calcium chloride and a small concentration of potassium metavanadate (catalyst). The precipitated calcium fluoride is separated, washed and weighed.)

The Equilibrium Composition at Various Concentrations in the System  $BF_8$ - $H_2O$  at 25°.—Accurately weighed quantities of pure boron trifluoride dihydrate were diluted with water to definite volumes and allowed to stand in sealed polyethylene bottles at room temperature for several months (equilibrium has been attained when the HBF<sub>4</sub> concentration has become constant). Fifteen mixtures of stoichiometric  $BF_3$  concentration from 0.005 to 15.6 *M* ( $BF_8$ : $2H_2O$ ) were thus prepared. Before analysis, the mixtures were maintained for two days at  $25^\circ \pm 0.1$ ; and in the case of all the mixtures in the concentration range 3.17 to 12.2 *M* (which contained boric acid as a solid phase), the slurries were mechanically stirred at  $25^\circ$  for 2 days.

The composition of the solutions up to 3 M was determined by direct analysis of aliquots by the previously described methods. All of these analyses can be performed quickly enough so that the original equilibrium relationships are preserved.

The method of analysis of those mixtures above 3 M was modified in two respects: (1) The mixtures containing precipitated boric acid were first filtered at 25°; and (2) in order to facilitate the analytical manipulation of these more concentrated solutions, and to prevent alteration of the original relationships of the various species, it was found necessary to dilute the sample for analysis by a special technique: Addition of the bulk sample to water can cause considerable shifting of the equilibrium, presumably because of the local heat effect in regions where the concentrated sample comes into contact with water. It was found that this effect could be completely obviated by introducing the sample as a fine stream through a capillary immersed in a large excess of water undergoing vigorous stirring. After the analyses have been performed, the amount of sample taken from the capillary may be determined by an analysis for either total boron or fluorine.

Figure 2 represents the concentration of the various species present at equilibrium at 25° for various stoichiometric concentrations of BF<sub>3</sub>. The concentrations of the several species at a given stoichiometric concentration of BF<sub>3</sub> are represented by the vertical intervals between the curves.



Fig. 2.—Composition of  $BF_3$ -H<sub>2</sub>O mixtures at equilibrium at  $25^{\circ}$ .

The Stability of  $BF_8 \cdot 2H_2O$ .—Of particular interest is the conclusion that  $BF_8 \cdot 2H_2O$  does not appear to be appreciably dissociated at 25°. It has been generally conceded that the dihydrate is a pure compound, at least below 6°, since it exhibits a

<sup>(10)</sup> I. G. Ryss, J. Gen. Chem. (U. S. S. R.), 16, 531 (1946).

<sup>(11)</sup> I. G. Ryss, Zavodskaya Lab., 12, 651 (1946).

sharp melting point maximum at this temperature.8 It is also characterized by a well-defined X-ray diffraction pattern similar to that of ammonium fluoborate,12 indicating a compound of the form H<sub>3</sub>O+-BF3OH-, i.e., hydronium monohydroxyfluoborate. However, certain experiments involving BF<sub>3</sub>·2H<sub>2</sub>O at temperatures above its melting point, have been interpreted as evidence for the dissociation in the liquid state into an equilibrium mixture of fluoboric acids. For example, cryoscopic measurements indicate that the dihydrate is dissociated in dioxane solution.8 However, anhydrous BF3 is known to form a coördination compound with dioxane<sup>13</sup> because of the electron donating character of the oxygen atom, and the following equilibrium is probably established

$$H_{3}O+BF_{3}OH^{-} + O(CH_{2}CH_{2})_{2}O \xleftarrow{} \\ [BF_{3}\leftarrow O(CH_{2}CH_{2})_{2}O] + 2H_{2}O$$

The water liberated from this reaction is probably responsible for the hydrolysis and consequent observed dissociation into other fluoboric acids, including HBF<sub>4</sub>. Similarly, if  $BF_{3}$ · $2H_2O$  is added to an excess of pyridine, some water is liberated in the formation of a  $BF_3$ -pyridine complex and the solution soon contains the hydro(tetra)fluoborate salt of pyridine as well as the hydro-monohydroxyfluoborate.

On the other hand, if  $BF_3 \cdot 2H_2O$  at  $25^{\circ}$  is introduced into an excess of rapidly stirred water by means of a capillary, the resultant solution is identical, with respect to conductance and analytical behavior, with an aqueous solution of HBF<sub>3</sub>OH (at the equivalent stoichiometric concn.) prepared either from  $B(OH)_3 + 3HF$  or by any of the methods described in a later section. Since such a solution shows no test for HBF<sub>4</sub>, and since pure BF<sub>3</sub>.  $2H_2O$  at  $25^{\circ}$  does not attack glass (indicating the absence of HF and thus indirectly the absence of other hydroxyfluoboric acids), it appears that the dihydrate at  $25^{\circ}$  is essentially pure  $H_3O+BF_3OH^-$ .

The monohydrate of boron trifluoride, corresponding to 20.2 M, is probably also a pure com-



Fig. 3.—Specific conductance at 25° of equilibrium mixtures from  $BF_8-H_2O$ 

(12) L. J. Klinkenberg and J. A. Ketelaar, Rec. trav. chim., 54, 959 (1935).

(13) H. Meerwein, Ber., 66B, 411 (1933).

pound at  $25^{\circ}$  (*i.e.*, anhydrous HBF<sub>3</sub>OH). Careful dilution with water as described above also yields a solution identical with an equivalent HBF<sub>3</sub>OH solution prepared by other methods.

Conductance of  $BF_3-H_2O$  Mixtures at Equilibrium.—Figure 3 is a plot of the specific conductances at 25° of the mixtures whose equilibrium composition had been determined. The maximum conductance occurs at about 5 M which also corresponds to the concentration at which the boric acid solubility appears to be a minimum. The linear decrease in conductance from  $BF_3 \cdot 2H_2O$  to  $BF_3 \cdot H_2O$ is probably associated with the corresponding dehydration of the hydrogen ion.

Electrometric Titration of Aqueous BF<sub>3</sub> Solution at Equilibrium.—Figure 4 represents a pH titration of 200 ml. of a solution of stoichiometric BF<sub>3</sub> concentration 0.158 M, at equilibrium, with 2.020 N NaOH. Analysis indicated the composition: 0.0937 M HBF<sub>4</sub>, 0.0331 M HBF<sub>3</sub>OH and 0.0327 M B(OH)<sub>3</sub>. If the hydroxyfluoboric acid group is represented as HBF<sub>3</sub>OH, the first inflection, at pH 3.2, corresponds accurately to the neutralization of [HBF<sub>4</sub> + HBF<sub>3</sub>OH]

 $HBF_4 + NaOH \longrightarrow NaBF_4 + H_2O$  (9.30 ml.)

$$HBF_{3}OH + NaOH \longrightarrow NaBF_{3}OH + H_{2}O$$
 (3.28 ml.)

From this point to the next inflection at pH 7.3, the following reaction is represented

 $NaBF_{3}OH + 2NaOH \longrightarrow 3NaF + B(OH)_{3} (6.56 ml.)$ 

From this point to the last inflection at  $\rho$ H 10.4, the boric acid originally present plus that liberated from the decomposition of the hydroxyfluoborates, is accurately represented (= 1/2 6.56 + 3.24 = 6.52 ml.)



Fig. 4.—pH titration of 200 ml. aqueous solution of boron trifluoride at equilibrium at 25° (0.158 *M* BF<sub>3</sub> stoich.) with 2.020 *N* NaOH.

Kinetics of the Reaction of  $BF_3$  and  $H_2O$ ; and the Hydrolysis Constant of  $HBF_3OH$ .—The clean-cut analytical distinction between  $HBF_4$  and  $HBF_3OH$  (on the basis of nitron precipitability) permits the ready evaluation of the hydrolysis constant of  $HBF_4$ .<sup>4</sup> However, the acids  $HBF_3OH$  and  $HBF_2(OH)_2$  do not exhibit such analytical distinction; further, *in situ* measurements, such as conductance, can offer only qualitative evidence of the hydrolysis of HBF<sub>3</sub>OH, since the relative strengths of the acids involved are not known. However, kinetic considerations should offer a reasonable approach to the evaluation of the hydrolysis constant of HBF<sub>3</sub>OH, since the kinetics of the rate-controlling step are dependent upon the concentrations of HBF<sub>3</sub>OH and HF, which in turn are controlled by the extent of the hydrolysis of the HBF<sub>3</sub>OH. The product of the rate-controlling step is HBF<sub>4</sub>, which is readily determined by direct analysis.

When boron trifluoride reacts with water, the equilibria in the solution at time t = 0 may be represented as

$$HBF_{3}OH + H_{2}O \xrightarrow{\text{rapid}} HBF_{2}(OH)_{2} + HF$$

$$+$$

$$H_{2}O$$

$$\uparrow \downarrow \text{rapid}$$

$$HBF(OH)_{3} \xrightarrow{\text{rapid}} B(OH)_{3} + HF$$

$$+$$

$$HF$$

Most of the HF in the solution at t = 0 may be regarded as being derived from HBF<sub>3</sub>OH, since the hydrolysis of HBF<sub>2</sub>(OH)<sub>2</sub> is slight at the start. However, as the reaction proceeds

$$HBF_{3}OH + HF$$
 (slow)  $HBF_{4} + H_{2}O$ 

and HBF<sub>3</sub>OH and HF are withdrawn in the formation of the very stable HBF<sub>4</sub>, there is a continual shifting of the equilibria depicted above in the direction of  $B(OH)_3$  (the solution at equilibrium contains a considerable concentration of boric acid). That is, as HF is removed in the slow formation of HBF<sub>4</sub>, it is rapidly replaced at the expense of the degradation of the hydroxyfluoboric acids toward boric acid, so that there is a tendency for the concentration of HF to be maintained at its initial value, at least in some of the earlier part of the reaction (the concentration of HF eventually falls off to zero at equilibrium).

An assumption which will permit the quantitative solution of this kinetic system is that, for the early stages of the reaction, the concentration of HF changes slowly with time so that as a close approximation d[HF]/dt = 0.

The kinetics of the net reaction of  $BF_3$  and  $H_2O$  is of the type of consecutive reactions represented by the general system

$$A \underset{k_1}{\overset{k_1}{\underset{k_1}{\longleftarrow}}} B + C \text{ (rapid)}$$

$$A + B \xrightarrow{n_2} D$$
 (slow, rate-determining)

where  $A = HBF_3OH$ , B = HF,  $C = HBF_2(OH)_2$ and  $D = HBF_4$ .

The general case of this type has recently been discussed by Hirschfelder and Boyd.<sup>14</sup> The expression for the rate constant  $k_2$  was derived as shown

$$d[A]/dt = -k_1[A] + k_1'[B][C] - k_2[A][B]d[B]/dt = k_1[A] - k_1'[B][C] - k_2[A][B]d[D]/dt = k_2[A][B]$$

If as an approximating assumption (for the early stages of the reaction only)  $d[\mathbf{B}]/dt = 0$ 

Then

$$d[A]/dt = -2 d[D]/dt = -2 k_2[A][B]$$

For a solution of stoichiometric BF<sub>3</sub> concentration M moles/liter, the initial concentrations of [HBF<sub>3</sub>OH] and [HF] are determined by the degree of hydrolysis  $\alpha$  of HBF<sub>3</sub>OH at time t = 0; *i.e.* 

$$K_{\rm eq.} = \frac{k_1}{k_1'} = \frac{[{\rm HBF}_2({\rm OH})_2][{\rm HF}]}{[{\rm HBF}_3{\rm OH}]} = \frac{M\alpha_0^2}{1-\alpha_0} \quad (5)$$

and

$$[HBF_3OH] = M(1 - \alpha_0) \text{ at } t = 0, \text{ but at any time } t \text{ is given} \\ \text{by } M(1 - \alpha_0) - x \text{ where } x \text{ is the concentra-tion of HBF_3OH consumed at time } t.$$

 $[HF] = M\alpha_0$  at t = 0 and approximately the same value for any time t in the early stages of the reaction.

$$[\text{HBF}_2(\text{OH})_2] = M\alpha_0 \text{ at } t = 0, \text{ but at any time } t \text{ is given by}$$
$$\frac{k_1[\text{HBF}_3\text{OH}] - k_2[\text{HBF}_3\text{OH}][\text{HF}]}{k_1'[\text{HF}]}$$

Then since

$$d[HBF_{3}OH]/dt = -2k_{2}[HBF_{3}OH][HF] \\ k_{2} = \frac{2.303}{2M\alpha_{0}t} \log \frac{M(1-\alpha_{0})}{M(1-\alpha_{0})-x}$$
(6)

This reaction is thus characterized as essentially first order.

Before  $k_2$  can be evaluated from experimental data, the value of  $\alpha_0$  or  $K_{eq.}$  for the hydrolysis of HBF<sub>3</sub>OH must be determined. This was obtained from additional kinetic data as follows:

If solutions of HBF<sub>3</sub>OH (at a given constant stoichiometric concentration of  $BF_3$ ) are treated with measured excesses of HF, the kinetics may be treated directly as second order if  $[HF] \ge [HBF_3]$ -OH]. This is verified by the consistent interpretation of experimental kinetic data which results from such treatment. For the case: added HF = 0, the treatment is first order for the early stages, probably changing toward second order, while for intermediate cases (added HF from 0 to [HBF3-OH]), the reaction is probably to be regarded as changing more rapidly from first to second order as added HF approaches [HBF $_3$ OH]. The *p*H curve of Fig. 1 indicates that the hydrogen ion activity of all the solutions will be practically identical. If Mis the stoichiometric concn. of  $BF_{\delta}$  and y is the concn. of HF added, and the initial concentrations of HBF<sub>3</sub>OH and HF are taken as  $M(1 - \alpha_0)$  and  $(y + M\alpha_0)$ , respectively, (where  $\alpha_0$  is the degree of hydrolysis of HBF<sub>3</sub>OH in the presence of HF when added in concentration y), then the rate constant becomes

$$k_2 = \frac{2.303}{t[y - M(1 - 2\alpha_0)]} \log \frac{M(1 - \alpha_0)(y + M\alpha_0 - x)}{(y + M\alpha_0)(M - M\alpha_0 - x)}$$
(7)

Analysis of an aliquot of the reaction mixture at various times t for [HBF<sub>4</sub>] affords a direct measure of x. For a series of systems [MHBF<sub>3</sub>OH + yHF] investigated experimentally, there is a series of  $\alpha_0$  values corresponding to the various y values which satisfy two conditions

<sup>(14)</sup> J. O. Hirschfelder and C. A. Boyd, J. Chem. Educ., 27, 127 (1950).

C

A

(1) 
$$\frac{[\text{HBF}_2(\text{OH})_2][\text{HF}]}{[\text{HBF}_2\text{OH}]} = \frac{M\alpha_0(y + M\alpha_0)}{M(1 - \alpha_0)} = a \text{ constant} = K_{eq.} \quad (8)$$

(2) The rate constant  $k_2$  calculated from equation (7) is the same for each value of y.

Accordingly, the kinetics of three systems at M = 0.0561 were studied: [HBF<sub>3</sub>OH + HF], [HBF<sub>3</sub>OH + 2 HF] and [HBF<sub>3</sub>OH + 5.5 HF] (corresponding to y = 0.0561, 0.1102 and 0.3085, respectively).

The proper quantity of boric acid dissolved in water in a polystyrene volumetric flask, was treated with the appropriate amount of dilute aqueous hydrofluoric acid, the mixture diluted to definite volume, and maintained at  $25^{\circ} \pm 0.1$  in a thermostated bath. At recorded time intervals, aliquots were withdrawn and analyzed for HBF<sub>4</sub>.

The best values of  $\alpha_0$  that satisfied the conditions described above were 3, 8 and 14% (for y = 0.3085, 0.1102 and 0.0561, resp.). The corresponding rate constants were 0.246, 0.250 and 0.242 liter moles<sup>-1</sup> min.<sup>-1</sup>. This establishes the value of the equilibrium constant  $K_{\text{eq.}}$  for the hydrolysis of HBF<sub>3</sub>OH according to equation (8) as 0.011 at 25°.

From equation (5) then, the degree of hydrolysis  $\alpha_0$  for HBF<sub>3</sub>OH in water at stoichiometric conen. M = 0.0561, becomes 35%, and the value of the rate constant for the system [HBF<sub>3</sub>OH + H<sub>2</sub>O] (*i.e.*, y = 0) determined from equation (6) becomes 0.244 liter moles<sup>-1</sup> min.<sup>-1</sup> (Table I). This is in close agreement with the rate constants determined for the other three systems (average 0.246), thus affording experimental evidence that the reaction of boron trifluoride with water is controlled kinetically by reaction (4).

Thus, the two quite different kinetic treatments, in which [HF] is regarded as nearly constant when it is small (Case 4, Table I), but as a variable when it is relatively large, (Cases 1, 2, 3, Table I) result in essentially the same value of the rate constant, and this may hence be regarded as providing evidence of their validity. As will be indicated later, this concordance of rate constant determinations was also obtained at other concentrations.



Fig. 5. - Relation between H ion activity and rate constant.

TABLE I

KINETIC DATA FOR FOUR SYSTEMS: 0.0561 M HBF<sub>3</sub>OH +  $\gamma M$  HF

| t in min.<br>1) [HBF <sub>1</sub> O<br>oncn. [HBF <sub>1</sub><br>Miquot taken<br>t equilibrium | $\begin{array}{l} \text{M1. 0.1021 } N \\ \text{NaOH} \approx \\ \text{HBF}_{4} \\ \text{OH} + 5.5 \text{ HI} \\ \text{sOH} \end{bmatrix} = 0.04 \\ \text{n for analysi} \\ \text{m: } 0.0554 \\ 0. \\ \end{array}$ | x, concn. of<br>HBF <sub>1</sub> OH con-<br>sumed at t<br>F]: $y = 0.308i$<br>544; initial cor<br>s, 50 ml. Con<br>M HBF <sub>4</sub> , 0.000<br>253 M HF. | k2, rate constant<br>(from eq. 7 for<br>systems 1, 2, 3;<br>from eq. 6 for<br>system 4)<br>liter moles <sup>-1</sup> min<br>5; $\alpha_0 = 3\%$ ; init<br>aposition of soluti<br>07 M HBF <sub>3</sub> OH a | ial<br>D2.<br>Ion<br>nd |
|---|---|--|---|-------------------------|
| 7.0   | 10.67   | 0.0218   | 0.245   |                         |
| 10 5  | 10 54   | 0000   | 047   |                         |

|      | ~~    | 0.00  | 00   |       |
|------|-------|-------|------|-------|
| 13.5 | 16.54 | .0338 | .247 |       |
| 21.3 | 20.67 | .0422 | .247 | 0.246 |
| 30.8 | 23.25 | .0475 | .241 |       |
| 54.7 | 25.92 | .0530 | .248 |       |
| 92.0 | 26.93 | .0550 |      |       |

(2) [HBF<sub>3</sub>OH + 2HF]: y = 0.1122;  $\alpha_0 = 8\%$ ; initial concn. [HBF<sub>3</sub>OH] = 0.0516; initial concn. [HF] = 0.1167. Aliquot taken for analysis, 50 ml. Composition of solution at equilibrium: 0.0535 *M* HBF<sub>4</sub>, 0.0026 *M* HBF<sub>3</sub>OH and 0.0587 *M* HF.

|      | 0.0   | 1007 IN III. |       |       |
|------|-------|--------------|-------|-------|
| 12.1 | 7.14  | 0.0146       | 0.252 |       |
| 25.0 | 12.03 | .0246        | .251  |       |
| 41.7 | 15.92 | .0325        | .246  | 0.950 |
| 50.2 | 17.50 | .0357        | .249  | 0.200 |
| 61.5 | 19.32 | .0395        | .250  |       |
| 114  | 22.92 | .0468        | .251  |       |
| 158  | 24.63 | .0503        |       |       |

(3) [HBF<sub>3</sub>OH + HF]: y = 0.0561;  $\alpha_0 = 14\%$ ; initial concn. [HBF<sub>3</sub>OH] = 0.0430; initial concn. [HF] = 0.0640. Aliquot taken for analysis, 50 ml. Composition of solution at equilibrium: 0.0463 *M* HBF<sub>4</sub>, 0.0098 *M* HBF<sub>3</sub>OH and 0.0098 *M* HF.

| 1.81  | 0.0037   | 0.240  |
|-------|--|--|
| 4.65  | .0095  | .242   |
| 7.72  | .0158  | $.246 \\ 0.242$  |
| 10.27 | .0210  | .242   |
| 12.04 | .0246  | .239   |
| 15.18 | .0310  | .236   |
| 18.80 | .0384  | .230   |
|       | $1.81 \\ 4.65 \\ 7.72 \\ 10.27 \\ 12.04 \\ 15.18 \\ 18.80$ | $\begin{array}{ccccccc} 1.81 & 0.0037 \\ 4.65 & .0095 \\ 7.72 & .0158 \\ 10.27 & .0210 \\ 12.04 & .0246 \\ 15.18 & .0310 \\ 18.80 & .0384 \end{array}$ |

(4) [HBF<sub>3</sub>OH in water]: y = 0;  $\alpha_0 = 35\%$ ; initial concn. [HBF<sub>3</sub>OH] = 0.0365; initial concn. [HF] = 0.0196. Aliquot taken for analysis, 100 ml. Composition of solution at equilibrium: 0.0318 *M* HBF<sub>4</sub>, 0.0078 *M* HBF<sub>3</sub>OH, 0.0088 *M* HBF<sub>2</sub>(OH)<sub>2</sub>, 0.0077 *M* B(OH)<sub>3</sub>.

| 9.0  | 3.02  | 0.0031 | 0.247           |
|------|-------|--------|-----------------|
| 15.2 | 4.85  | .0049  | $.241 \\ 0.244$ |
| 21.6 | 6.68  | .0068  | .244 )          |
| 30.5 | 8.81  | .0090  | .235            |
| 40.4 | 10.38 | .0106  | .216            |
| 66.0 | 14.80 | .0151  | .207            |

The kinetic investigations were extended to other concentrations and Table II lists the rate constants obtained.

The rate constant for the over-all reaction of boron trifluoride and water was found to be a linear function of the hydrogen ion activity (Fig. 5), indicating that the reaction is acid-catalyzed. The equation of the line is

$$k = k_0 + k_{\rm H}[{\rm H^+}]$$

in which  $k_0$  is the rate constant of the "spontaneous reaction" = 0.064 liter moles<sup>-1</sup> min.<sup>-1</sup> and  $k_H = 7.35$ .

It was further established that the rate constant obtained at 0.0561 M could be increased to that ob-

| TABLE ] | 11 |
|---------|----|
|---------|----|

VARIATION OF RATE CONSTANT WITH (STOICH.) BF, CON-CENTRATION

| Stoich. conen. BF:<br>in mole/liter | k; at 25°,<br>liter moles <sup>-1</sup> min. <sup>-1</sup> | <i>p</i> H at 25° |
|-------------------------------------|--|-------------------|
| 0.0150                              | 0.098  | 2.24              |
| .0561                               | .244   | 1.65              |
| .110                                | .387   | 1.36              |
| .208                                | .635   | 1.10              |

tained at 0.208 M by the addition of sufficient hydrochloric acid to 0.0561 M HBF<sub>3</sub>OH to lower the  $\rho$ H to 1.10.

The  $\alpha_0$  values obtained at the concentrations other than 0.0561 M were consistent with the hydrolysis constant for HBF<sub>3</sub>OH previously evaluated from kinetic data at 0.0561 M. Further, all the rate constants calculated from eq. 7 (for systems of HBF<sub>3</sub>OH and added excess HF) were the same as the corresponding values calculated from eq. 6 (for the system HBF<sub>3</sub>OH-H<sub>2</sub>O), at all four of the chosen concentrations indicated in Table II, within the limits of experimental error.

The Concentration of  $HBF_2(OH)_2$  in the More Dilute  $BF_3$  Solutions.—If the equilibrium constants of the following hydrolysis reactions are combined

 $HBF_4 + H_2O \longrightarrow HBF_3OH + HF; K_{eq.} = 0.0023^4$ 

 $HBF_{3}OH + H_{2}O \longrightarrow HBF_{2}(OH)_{2} + HF; K_{eq.} = 0.011$ 

then

$$\frac{[\text{HBF}_{3}\text{OH}]^{2}}{[\text{HBF}_{4}][\text{HBF}_{2}(\text{OH})_{2}]} = 0.21$$

From this relation, the relative concentrations of  $HBF_2(OH)_2$  and  $HBF_3OH$  in the more dilute solutions may be estimated, since  $[HBF_4]$  and  $[HBF_2(OH)_2 + HBF_3OH]$  may be determined by analysis. The concentration of  $[HBF_2(OH)_2]$  thus obtained will include  $HBF(OH)_3$ .

The equilibrium composition of  $BF_3-H_2O$  mixtures in the concentration range 0.01 to 0.20 *M* are thus represented in Fig. 6. As in Fig. 2, the concentrations of the species are represented by the vertical intervals between the curves, at any given stoichiometric concentration of  $BF_3$ .



Fig. 6.—Composition of dilute aqueous BF<sub>3</sub> solutions at equilibrium at 25°.

The Conductances and Acid Strengths of the Fluoboric Acids.—The relative strengths of the fluoboric acids may be conveniently estimated by comparison of the conductances of aqueous solutions of the pure acids free from their hydrolysis products. However, this is experimentally realizable only for HBF<sub>4</sub> and HBF<sub>3</sub>OH. The conductance data represented in Fig. 7 were obtained as follows:



Fig. 7.—Specific conductance at  $25^{\circ}$  of aqueous solutions: O, HBF<sub>4</sub>;  $\bullet$ , HBF<sub>3</sub>OH;  $\bullet$ , HBF<sub>3</sub>OH in equilibrium with HBF<sub>2</sub>(OH)<sub>2</sub> + HF.

(A) HBF<sub>4</sub> Free from its Hydrolysis Products. —Such solutions were prepared by two methods: (1) by mixing solutions containing equivalent quantities of pure, recrystallized barium fluoborate dihydrate and sulfuric acid; and (2) by passing aqueous solutions of pure, recrystallized potassium fluoborate through a column of cation exchange resin in hydrogen form, *e.g.*, Amberlite IR-100H. The conductances of such solutions can easily be measured before the occurrence of any appreciable hydrolysis, which is kinetically slow.

(B) HBF<sub>3</sub>OH Free from its Hydrolysis Products.—This cannot be obtained by either of the methods mentioned under (A) since HBF<sub>3</sub>OH establishes hydrolytic equilibrium so rapidly. However, the desired data were obtained by performing a series of conductance titrations of the type illustrated in Fig. 1. At each concentration a conductance value corresponding to the point A of Fig. 1 was obtained by extrapolation.

(C) HBF<sub>3</sub>OH in Equilibrium with its Hydrolysis Products.—These data were obtained by a number of independent methods: (1) by measuring immediately the conductance of solutions prepared from  $B(OH)_3 + 3$  HF, *i.e.*, point B of Fig. 1; (2) by passing an aqueous solution of pure KBF<sub>3</sub>OH through a column of cation exchange resin in hydrogen form; and (3) by very careful direct introduction of pure  $BF_3 \cdot 2H_2O$  by means of a capillary into water.

These data indicate that HBF<sub>4</sub> and HBF<sub>3</sub>OH in aqueous solutions, are about as strong as HCl and CCl<sub>3</sub>COOH, respectively. Furthermore, HBF<sub>2</sub>-(OH)<sub>2</sub> in aqueous solution is approximately as strong as CHCl<sub>2</sub>COOH since the measured conductances of solutions of HBF<sub>3</sub>OH in equilibrium with HBF<sub>2</sub>(OH)<sub>2</sub> and HF are nearly identical with those of solutions of CCl<sub>3</sub>COOH, CHCl<sub>2</sub>COOH and HF in the appropriate proportional concentrations of  $M(1 - \alpha_0)$ ,  $M\alpha_0$  and  $M\alpha_0$ , respectively. The observed decrease in acid strength in the order HBF<sub>4</sub>  $\rightarrow$  HBF<sub>3</sub>OH  $\rightarrow$  HBF<sub>2</sub>(OH)<sub>2</sub>  $\rightarrow$  HBF-(OH)<sub>3</sub>  $\rightarrow$  B(OH)<sub>3</sub> may be explained by the changes in the electrostatic inductive effect of the anion on the proton as fluorine atoms are successively replaced by hydroxyl groups. The highly electronegative fluorine atoms attract electrons more strongly than oxygen atoms, so that the tendency for the proton to split off is greater for the fluoboric acids containing more fluorine. Further, the proton is probably held more firmly by a B-linked OH group than by a B-F unit.

FLUSHING, N. Y.

Received June 30, 1950

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF ARGONNE NATIONAL LABORATORY]

# The Preparation of Anhydrous Americium Compounds

#### By Sherman Fried

By use of techniques developed in the studies of the chemistry of the other heavy elements, it has been possible to prepare and identify several simple compounds of americium. With the exception of the dioxide,  $AmO_2$ , the compounds of americium prepared were in the III oxidation state, and the formulas  $AmF_3$ ,  $AmCl_3$ ,  $AmBr_3$ ,  $AmI_3$  and  $Am_2S_3$  may be considered analogous to the corresponding compounds of the rare earth series. A detailed description of the techniques and a qualitative discussion of the properties of americium is presented.

Americium, element number 95, was discovered by Seaborg, James and Morgan in plutonium irradiated in the chain reacting pile.<sup>1,2</sup> The reactions are

$$\operatorname{Pu}^{239}(n, \gamma) \operatorname{Pu}^{240}(n, \gamma) \operatorname{Pu}^{241} \xrightarrow{\beta^-} \operatorname{Am}^{241}$$

This isotope is an alpha emitter with a halflife of  $475 \pm 22$  years which was determined by weighing and counting samples of americium oxide.<sup>3,4</sup>

The isolation of americium in a relatively pure state was first accomplished by Cunningham who obtained a few micrograms of 99% pure material.<sup>4</sup>

Studies of the behavior of americium in aqueous solution by Cunningham have shown that its most prominent oxidation state is +3 and that in this state it closely resembles the tripositive rare earths. It differs, however, in that it has proved possible to oxidize it to the +5 state under certain conditions<sup>5</sup> and recently Asprey, Stephanou and Penneman have prepared the +6 "americyl" ion, AmO<sub>2</sub><sup>++</sup>, analogous to uranyl, neptunyl and plutonyl ions.<sup>6</sup>

The formal analogy of americium to the rare earths is more marked in the anhydrous compounds and it has been found that compounds of americium are isomorphous with corresponding compounds of some of the rare earths as well as with those of the transuranium elements.

(1) G. T. Seaborg, Chem. Eng. News, 24, 1193 (1946).

(2) A. Ghiorso, R. James, L. Morgan and G. T. Seaborg, Phys. Rev., 78, 472 (1950).

(3) B. B. Cunningham, S. Thompson and H. Lohr, unpublished work, 1949.

(4) B. B. Cunningham, "The Transuranium Elements," National Nuclear Energy Series, Vol. 14B, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, paper 19.2.

(5) L. B. Werner and I. Perlman, "The Transuranium Elements," National Nuclear Energy Series, Vol. 14B, McGraw-Hill Book Co.. Inc., New York, N. Y., 1949, Paper 22.5.

(6) L. B. Asprey, S. E. Stephanou and R. A. Penneman, THIS JOURNAL, 72, 1425 (1950).

This paper will describe the preparation of some of the solid compounds of americium and some qualitative relationships to the other heavy elements.

All of the compounds prepared were identified from their X-ray diffraction patterns by Prof. W. H. Zachariasen. This method has proved to be eminently successful in the identification of various compounds of actinium, neptunium and plutonium.

### Experimental

**Apparatus.**—Most of the compounds were prepared by techniques already described in the literature. In particular, the methods used for the preparation of microgram quantities of actinium, neptunium and plutonium were directly applicable.<sup>7,8</sup>

Americium Trifluoride.—Approximately fifty micrograms of americium Hydroxide was treated with a 1:1 hydrogen fluoride-oxygen mixture at 600-750° for 2 hours in an allplatinum hydrofluorination apparatus. The resulting pink product was shown to be the trifluoride,  $AmF_{2}$ , isomorphous with the corresponding trifluorides of uranium, neptunium and plutonium.<sup>9</sup>

The treatment of dioxides with hydrogen fluoride-oxygen mixtures leads to the formation of tetrafluorides in the cases of plutonium and neptunium, and the failure to obtain americium tetrafluoride under these conditions suggested the necessity of using fluorine to form this compound. Accordingly, samples of americium trifluoride were treated with free fluorine at one atmosphere pressure and temperatures varying from 500 to 700°. In no case was americium tetrafluoride formed.

Americium Dioxide.—This is the only known tetravalent compound of americium that has yet been isolated and identified in the solid state. It has been variously prepared by the ignition of the nitrate or hydroxide in air at approximately 1000°. The resulting oxide is black and appears to exhibit some variation in lattice dimensions depending upon the temperature of ignition.<sup>10</sup>

When the black americium oxide is dissolved in dilute hydrochloric acid it reacts to liberate bubbles of gas (chlo-

(9) W. H. Zachariasen, Acta Cryst., 2, 388 (1949).

<sup>(7)</sup> S. Fried and N. Davidson, THIS JOURNAL, 70, 3539 (1948).

<sup>(8)</sup> S. Fried, F. Hagemann and W. H. Zachariasen, *ibid.*, 72, 771 (1950).

<sup>(10)</sup> W. H. Zachariasen, CP-3497, April, 1946, p. 2.