

resin in hydrogen form; and (3) by very careful direct introduction of pure  $\text{BF}_3 \cdot 2\text{H}_2\text{O}$  by means of a capillary into water.

These data indicate that  $\text{HBF}_4$  and  $\text{HBF}_3\text{OH}$  in aqueous solutions, are about as strong as  $\text{HCl}$  and  $\text{CCl}_3\text{COOH}$ , respectively. Furthermore,  $\text{HBF}_2(\text{OH})_2$  in aqueous solution is approximately as strong as  $\text{CHCl}_2\text{COOH}$  since the measured conductances of solutions of  $\text{HBF}_3\text{OH}$  in equilibrium with  $\text{HBF}_2(\text{OH})_2$  and  $\text{HF}$  are nearly identical with those of solutions of  $\text{CCl}_3\text{COOH}$ ,  $\text{CHCl}_2\text{COOH}$  and  $\text{HF}$  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  $\text{HBF}_4 \rightarrow \text{HBF}_3\text{OH} \rightarrow \text{HBF}_2(\text{OH})_2 \rightarrow \text{HBF}(\text{OH})_3 \rightarrow \text{B}(\text{OH})_3$  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.

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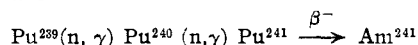
[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF ARGONNE NATIONAL LABORATORY]

## 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,  $\text{AmO}_2$ , the compounds of americium prepared were in the III oxidation state, and the formulas  $\text{AmF}_3$ ,  $\text{AmCl}_3$ ,  $\text{AmBr}_3$ ,  $\text{AmI}_3$  and  $\text{Am}_2\text{S}_3$  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



This isotope is an alpha emitter with a half-life 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,  $\text{AmO}_2^{++}$ , 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 all-platinum hydrofluorination apparatus. The resulting pink product was shown to be the trifluoride,  $\text{AmF}_3$ , 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-

(7) S. Fried and N. Davidson, *This Journal*, **70**, 3539 (1948).

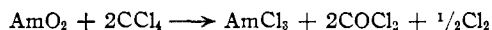
(8) S. Fried, F. Hagemann and W. H. Zachariasen, *ibid.*, **72**, 771 (1950).

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

(10) W. H. Zachariasen, *CP-3497*, April, 1946, p. 2.

rine or oxygen?), and at the same time swells to about ten times its original volume, becoming pink. The pink solid remains undissolved for some time, but after standing for several hours at room temperature in the acid solution, finally dissolves to form the usual pink solution of trivalent americium. The pink solid may be either the sesquioxide,  $\text{Am}_2\text{O}_3$  or the oxychloride,  $\text{AmOCl}$ .

**Americium Trichloride.**—This compound was prepared by the action of carbon tetrachloride vapor on americium dioxide at 800 to 900°



The apparatus was so arranged that a volatile reaction product sublimed out of the hot reaction zone and was condensed as a solid in a thin-walled quartz capillary.

In this case no sublimate appeared until the temperature of the furnace had reached 850°. At that temperature, a white material condensed just beyond the furnace. When sufficient solid had been collected, the capillary was sealed off and submitted for examination by X-ray diffraction methods. The sublimate was shown to be americium trichloride,  $\text{AmCl}_3$ .<sup>11</sup>

**Americium Tribromide.**—The general method of preparing tribromides, *i.e.*, the treatment of oxides with hydrogen bromide at elevated temperatures, has been found to be rather unsatisfactory for their preparation on the microgram scale. It has been shown that the reaction of anhydrous aluminum bromide with oxides or fluorides of the heavy elements yields the bromides of these elements in such a manner as to facilitate their separation and easy identification. This reaction not only may be applied to the preparation of bromides but also to the preparation of chlorides and iodides if the proper aluminum halide is employed. It has previously been successfully used in the preparation of the various halides of uranium, neptunium and plutonium. It may be remarked that this reaction is a very convenient method for the direct conversion of heavy element fluorides to the corresponding chloride, bromide or iodide. The probable reaction for americium dioxide is shown by the equation



A fifty-microgram sample of americium was precipitated from solution by addition of ammonia. The gelatinous precipitate was washed with water and dried in an oven at 150° for 3 hours. The resulting small fragment was placed in a quartz X-ray capillary together with approximately 150 micrograms of aluminum metal. The capillary was then connected to a vacuum line by means of the ground joint from which it was made and, after evacuation, pure bromine vapor was admitted onto the mixture of aluminum and americium which was heated to 200°. As the aluminum bromide was formed by the action of bromine on the aluminum it distilled into a cooler portion of the tube where it condensed as a solid slug. The capillary was sealed off in vacuum to a length of five inches, placed in a heavy-walled glass tube which in turn was sealed with one atmosphere of air inside, and finally the "bomb" assembly placed in a steel jacket, loosely capped at both ends. The whole system was heated to 500° for 8 hours. The apparatus is sketched in Fig. 1.

At the end of the heating period, the steel tube was opened and the capillary was removed from its glass jacket. It was found to contain a brownish melt, probably consisting of aluminum bromide, unreacted americium oxide, bromine and americium tribromide. The products of this reaction were separated by fractional sublimation in a vacuum.<sup>12</sup> After the excess aluminum bromide and bromine had distilled out at 200°, the americium bromide was sublimed at 850 to 900° and collected as a white solid in a cool portion of the capillary. It was identified as the tribromide,  $\text{AmBr}_3$ , isomorphous with  $\text{PuBr}_3$ , by the X-ray method.<sup>13</sup>

**Americium Triiodide.**—The preparation of this compound was carried out by a reaction similar to that used for the preparation of americium tribromide, *i.e.*, by action of a

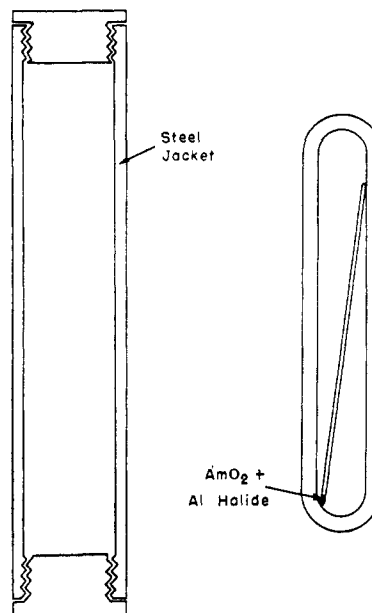


Fig. 1.

mixture of aluminum metal and iodine on the oxide of americium. The components were heated together in a quartz X-ray capillary bomb at 500° as described above. The reaction products were separated by fractional sublimation. A yellowish compound volatile at about 900° condensed in the cool portion of the tube. It was shown by the X-ray diffraction method to be americium triiodide,  $\text{AmI}_3$ , isomorphous with  $\text{NpI}_3$  and  $\text{PuI}_3$ .<sup>13</sup>

**Americium Sulfide.**—The sulfides of the heavy elements must be prepared in the dry way. Thus the reaction of neptunium oxide with hydrogen sulfide-carbon disulfide mixtures at 1000° gives rise to neptunium oxysulfide,  $\text{NpOS}$  and neptunium sesquisulfide,  $\text{Np}_2\text{S}_3$ ; with plutonium the products are  $\text{Pu}_2\text{O}_2\text{S}$  and  $\text{Pu}_2\text{S}_3$ . A sample of americium dioxide was placed in a quartz boat surrounded by a quartz tube which was heated by an electric furnace. Hydrogen sulfide which had been bubbled through carbon disulfide was passed over the oxide at 1000° for several hours. The compound resulting from this treatment gave an X-ray diffraction pattern unlike those given by the sulfides previously referred to. These patterns have not yet been interpreted.

When a twenty-microgram sample of americium dioxide in a graphite crucible was treated with a hydrogen sulfide-carbon disulfide mixture at a temperature of 1400–1500° for 5 minutes in an induction furnace, the product was shown by X-ray diffraction to be americium sesquisulfide,  $\text{Am}_2\text{S}_3$ , isomorphous with  $\text{La}_2\text{S}_3$ .<sup>13</sup>

**Americium Hydroxide.**—When a solution containing trivalent americium is treated with bases such as sodium or ammonium hydroxide, a pink gelatinous mass precipitates. Attempts to obtain X-ray diffraction patterns from dried samples of this material have failed. Lanthanum hydroxide prepared under these conditions yields an interpretable X-ray diffraction pattern.

## Discussion

The observations listed are largely descriptive in nature and do not lend themselves to quantitative consideration. Deductions as to the vapor pressures, melting points, etc., of the compounds described can only be comparative. Thus it would be expected that the solubilities of the various americium compounds in solvents would be similar to those of the corresponding compounds of neptunium, plutonium and the rare earths, and the melting points of the various americium halides would be expected to lie close to those of the rare earth halides.

(11) W. H. Zachariasen, *J. Chem. Phys.*, **16**, 254 (1948).

(12) S. Fried, F. Hagemann and W. H. Zachariasen, *THIS JOURNAL*, **72**, 773 (1950). It was found necessary to use this apparatus for carrying out the fractional sublimation because considerable gas pressures are developed in the course of the reaction. These gases interfere and must be removed.

(13) W. H. Zachariasen, *Acta Cryst.*, **1**, 265 (1948).

The most prominent oxidation state of americium in anhydrous compounds is the III state, with only one example each of the IV and VI states. In solution, an additional state, the V, can be formed. This is in agreement with the general observation that the ease of oxidation of the transuranium elements to higher states is in part due to the stabilization by oxygenation to form ions of the type  $\text{MO}_2^+$  and  $\text{MO}_2^{++}$  and to solvation by oxygenated solvents.

It seems unlikely that the anhydrous tetravalent chloride, bromide or iodide of americium can be prepared in view of the fact that no such compounds of plutonium have as yet been made. This would be in agreement with the observation that the III oxidation state becomes more prominent as the atomic number increases. It is possible, on the other hand, that the tetrafluoride may yet be prepared by the action of free fluorine or other vigorous fluorinating agents, in spite of the fact that several experiments in that direction have failed.

In most cases the X-ray diffraction pattern of the

compounds was obtained from samples weighing only a few micrograms. Generally, it would be more satisfactory to use samples up to one hundred micrograms but it was found that a fairly penetrating electromagnetic radiation emitted by the samples tended to fog the X-ray film. The rather unusual situation of having too much material made it necessary to restrict the quantities to the order of ten micrograms, which seemed to be the optimum amount. The effect of fogging of the X-ray film is naturally much more noticeable in the case of compounds exhibiting low symmetry where the original intensity of the beam is distributed over many diffraction lines.

**Acknowledgment.**—The author wishes to take this opportunity to express his indebtedness to Prof. W. H. Zachariassen for his interest in this work and his analyses of the americium compounds, without which this investigation would have been impossible.

CHICAGO, ILLINOIS

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[CONTRIBUTION FROM THE LEWIS FLIGHT PROPULSION LABORATORY OF THE NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS]

## Flame Propagation. II. The Determination of Fundamental Burning Velocities of Hydrocarbons by a Revised Tube Method

BY MELVIN GERSTEIN, OSCAR LEVINE AND EDGAR L. WONG

A method is described for the determination of fundamental rates of flame propagation in tubes. Data are presented for a variety of hydrocarbons including normal and branched alkanes, alkenes and alkynes as well as cyclohexane and benzene. The normal alkanes have a constant flame velocity except for methane which is slightly lower. Unsaturation increases the flame velocity in the order: alkanes < alkenes < alkynes. Branching reduces the flame velocity although the effect is small.

### Introduction

The high velocity combustion required in modern aircraft power plants has led to revived interest in the study of rates of flame propagation. As part of our fundamental combustion program an investigation was undertaken to determine the rate of flame propagation in gaseous mixtures of a variety of hydrocarbons and air as a function of molecular structure. A study of the relationship between fundamental rate of flame propagation and unsaturation, chain length and chain branching of hydrocarbons is reported.

Coward and Hartwell<sup>1</sup> developed a method for obtaining fundamental flame velocities in a tube by photographing the flame and computing its surface area. Coward and Payman<sup>2</sup> related the fundamental flame velocity  $U_f$  to the linear observed flame velocity  $U_0$  by the equation

$$U_f = (U_0 - U_g)A_i/A_f \quad (1)$$

where  $U_g$  is the velocity of the unburned gas ahead of the flame,  $A_i$  is the cross-sectional area of the tube and  $A_f$  is the surface area of the flame. The fundamental velocity  $U_f$  is that velocity component normal to any tangent to the flame surface. It is a function of hydrocarbon type and concentration but is independent of the experi-

mental apparatus. Because of the difficulty involved in its measurement, the gas velocity term was assumed to be negligible by earlier investigators using the tube method.

Attempts to reproduce the Coward and Hartwell method were only moderately successful. In the early phases of this research,<sup>3,4</sup> a Pyrex tube 12 feet long and 1 inch in diameter was used as the flame tube. Although it was possible to obtain relative trends in a hydrocarbon series using this technique, the results were dependent on the apparatus. The uniform flame movement over which the measurements were made occurred in only a small portion of the tube. The exact location of this uniform movement could not be predetermined for any particular hydrocarbon type. Moreover, the flame shape changed with hydrocarbon concentration so that the observed velocities were not proportional to the fundamental flame velocity. The uncertainty of the method is illustrated by the data of Wheatley<sup>5</sup> who reported the change in flame shape and was confirmed by preliminary experiments by the authors.

Guenoche, Manson and Mannot,<sup>6</sup> have demon-

(3) Reynolds and Gerstein, "Third Symposium on Combustion and Flame and Explosion Phenomena," The Williams and Wilkins Co., Baltimore, Md., 1949, p. 190.

(4) Reynolds and Ebersole, NACA Technical Note No. 1609 (1948).

(5) Wheatley, *Fuel*, **29**, 80 (1950).

(6) Guenoche, Manson and Mannot, *Compt. rend.*, **226**, 163 (1948).

(1) Coward and Hartwell, *J. Chem. Soc.*, Pt. II, pp. 2676-2684 (1932).

(2) Coward and Payman, *Chem. Rev.*, **21**, 359 (1937).