figuration using convenient, though chemically reactive, materials, Heretofore, this state has been available only in the rare and radioactive promethium(III) compounds. In this connection, Sheppard, *et al.*,[14] have recently made the difficult measurement of the susceptibility of $^{147}Pm^{3+}$ in the oxide at room temperature. Their result of 2780×10^{-6} erg gauss^{-2} mole^{-1} for χ_M (298°) (corrected for core diamagnetism) compares with an average of 3720×10^{-6} obtained here with the isoelectronic Nd^{2+} and a 2980×10^{-6} value calculated from the theoretical moment with the questionable assumption of $\Delta E >> kT$ (and $\Delta \sim 0$). It should be noted that population of the first excited state will *increase* χ_M. In the dihalides this thermal effect is about $(290 \pm 60) \times 10^{-6}$ e.s.u. in χ_M at room temperature, and it would be expected to be somewhat less for Pm^{3+} on the basis of $\Delta E/k \sim 2300$°K. estimated from analogous values for the neighboring, tripositive ions.[11,13] The difference observed for χ_M for Pm^{3+} may be due either to an effective moment that is lower than theory or to a significant self-heating of the sample.

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Protactinium Fluorides[1]

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Several protactinium fluorides have been prepared with 5 to 200 mg. amounts of Pa^{231}. The tetrafluoride, PaF_4, is a dark brown compound, isomorphous with UF_4 (monoclinic crystal structure), nonvolatile under vacuum up to 800°, and virtually insoluble in water and mineral acids. Protactinium pentafluoride, PaF_5, is a white compound, isomorphous with the β form of UF_5 (tetragonal crystal structure), soluble in aqueous hydrofluoric acid. The pentafluoride is much less volatile than its homologs VF_5, NbF_5, and TaF_5, but sublimes or distils under vacuum above 500°. A pentafluoride hydrate of approximate composition $PaF_5 \cdot 2H_2O$ is obtained as colorless, needle-like crystals on evaporation of solutions of protactinium in concentrated hydrofluoric acid. The hydrate decomposes at 160°, forming an oxyfluoride, Pa_2OF_8, which is white, isomorphous with U_2F_9 (body-centered cubic structure), and slightly volatile under vacuum above 500°. The oxyfluoride may also be prepared by several other methods.

Introduction

In the earliest studies of protactinium fluorides, Grosse[2] prepared the double fluoride with potassium, K_2PaF_7, and a pentafluoride hydrate of unspecified composition. A double fluoride with ammonium was reported by Emmanuel–Zavizziano[3] and subsequently a double fluoride with barium was described by Golden and Maddock.[4] Sellers, Fried, Elson, and Zachariasen[5] prepared the tetrafluoride, PaF_4, by hydrofluorination of PaO_2 and reported it to be isomorphous with ThF_4, UF_4, and PuF_4. Haissinsky and Bouissieres[6] reduced Pa(V) in a fluoride solution and obtained a white precipitate which was also believed to be protactinium tetrafluoride.

Very little information is found in the literature concerning volatile fluorides or oxyfluorides of protactinium. Emeléus, Maddock, Miles, and Sharpe[7] heated tracer quantities of Pa^{233} and Pa^{231} with bromine trifluoride but found no indication that a volatile fluoride was formed. At Brookhaven National Laboratory, the distillation of tracer Pa^{233} from neutron-irradiated ThF_4 was studied.[8] When the ThF_4 was strongly heated in a stream of fluorine or chlorine trifluoride, a slightly volatile protactinium compound was formed which condensed below 500°. Sellers, Fried, Elson, and Zachariasen[5] reported the formation of a volatile protactinium fluoride or oxyfluoride on heating protactinium oxide to 600° with either bromine trifluoride or bromine pentafluoride. Their product distilled under vacuum at 150° but subsequently decomposed, either by hydrolysis or reaction with the quartz vessel.

The present study reveals that a slightly volatile oxyfluoride, Pa_2OF_8, is formed under a variety of conditions. Several reactions useful for the preparation of the oxyfluoride, tetrafluoride, pentafluoride, and hydrated pentafluoride are reported.

Experimental

Protactinium-231 in the form of the hydrated pentoxide was obtained from the Atomic Energy Research Establishment, Harwell, England. In most experiments, the oxide was used without further purification, since spectrographic analyses indi-

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission and the U. K. Atomic Energy Authority.

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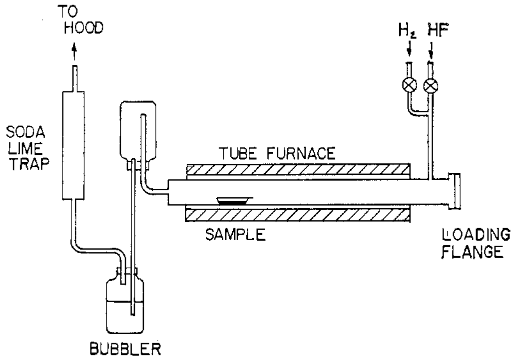

Fig. 1.—Hydrofluorination apparatus.

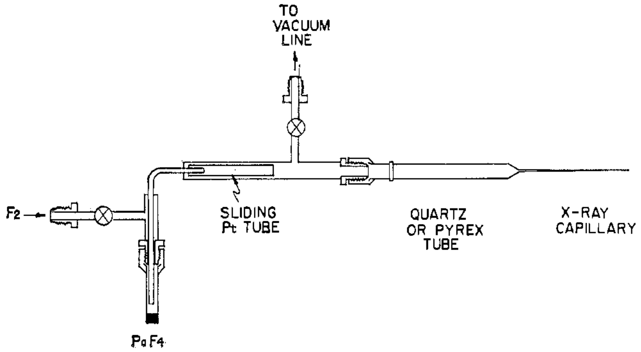

Fig. 2.—Fluorination apparatus.

cated the initial purity to be 99.7%.[9] Recently it was found that this material contains approximately 4% niobium,[10] which was overlooked in the very complex spectrum of protactinium. Although the niobium impurity is believed to have little effect on the preparative reactions described here, it introduces an error of approximately 0.5% in the composition of each protactinium fluoride, assuming that the niobium is not removed as NbF_5 in a distillation step. The results of the chemical analyses are compared in each instance with the required composition of the pure compound, with no correction for niobium.

PaF_4.—Protactinium tetrafluoride was prepared by heating the pentoxide in an approximately equimolar mixture of hydrogen and hydrogen fluoride, using the apparatus shown in Fig. 1. The Pa_2O_5 was contained in a platinum boat inside a nickel furnace tube. The gas mixture flowed through the tube, then through a polyethylene catch bottle and bubbler containing 48% hydrofluoric acid, the bubbler serving as a flow meter.

The furnace was heated gradually to 500° and maintained at that temperature for 2 hr. During cooling, the system was flushed with hydrogen alone. In four experiments, 20 to 230 mg. quantities of PaF_4 were prepared. (In one experiment, in which the temperature was allowed to rise quickly to 700°, most of the protactinium volatilized, presumably as the oxyfluoride, before reduction could occur.) The hydrofluorination reaction is

$$Pa_2O_5(s) + 8HF(g) + H_2(g) \xrightarrow[500°]{} 2PaF_4(s) + 5H_2O(g) \quad (1)$$

The tetrafluoride was analyzed by pyrohydrolysis and α-pulse analysis, as described below. *Anal.* Calcd. for PaF_4: Pa, 75.2; F, 24.8. Found: Pa, 75.2; F, 24.5, 25.3.

PaF_5.—Protactinium pentafluoride was prepared by heating PaF_4 to 700° with fluorine (eq. 2), using the apparatus shown in

$$PaF_4(s) + {}^1/_2F_2(g) \xrightarrow[700°]{} PaF_5(s) \quad (2)$$

Fig. 2. The PaF_4 was contained in a nickel test tube through which the fluorine gas flowed at a slow rate. The slightly volatile product condensed first in the nickel exit line, where it was detected with an external β–γ meter by the γ emission of Pa^{231}. The system was then evacuated, and the exit line was flamed with a torch to move the product into a sliding platinum tube (previously weighed). It was necessary to repeat the fluorination–evacuation process several times to move most of the γ activity from its original site to the platinum tube. (To avoid the formation of platinum fluorides, the flaming operation was carried out only in the absence of fluorine.) The tube containing the product was moved into the adjacent quartz or Pyrex section, which was sealed off with a torch and later reopened in a glove box.

In five experiments, 8 to 20 mg. quantities of PaF_4 were fluorinated. Two grades of fluorine were used, one of 99.9% purity, obtained by low-temperature distillation,[11] and the other a commercial grade of approximately 99% purity, containing small amounts of oxygen, nitrogen, carbon dioxide, hydrogen fluoride, and carbon tetrafluoride. When the purified fluorine was used, PaF_5 was obtained as the product in yields of 40 to 95%. *Anal.* Calcd. for PaF_5: Pa, 70.9; F, 29.1. Found: Pa, 69.5, 72.0; F, 30.2.

Pa_2OF_8.—In two instances in which PaF_4 was heated to 600° with commercial grade fluorine, the product was shown by X-ray powder patterns to be cubic rather than tetragonal. The cubic compound was subsequently identified as the oxyfluoride Pa_2OF_8. Its presence under these conditions can be attributed to either oxygen impurity in the fluorine, producing reaction 3, or to partial hydrolysis of PaF_5, shown in reaction 4. It was found

$$2PaF_4(s) + {}^1/_2O_2(g) \xrightarrow[600°]{F_2} Pa_2OF_8(s) \quad (3)$$

$$2PaF_5(s) + H_2O(g) \longrightarrow Pa_2OF_8(s) + 2HF(g) \quad (4)$$

that the oxyfluoride could also be prepared by heating Pa_2O_5 with fluorine or with an equimolar mixture of hydrogen fluoride and oxygen. The reactions are believed to be as follows (gaseous products not analyzed)

$$Pa_2O_5(s) + 4F_2(g) \xrightarrow[550°]{} Pa_2OF_8(s) + 2O_2(g) \quad (5)$$

$$Pa_2O_5(s) + 8HF(g) \xrightarrow[500°]{} Pa_2OF_8(s) + 4H_2O(g) \quad (6)$$

The thermal decomposition of $PaF_5 \cdot 2H_2O$ (see below) also yields Pa_2OF_8. A total of 140 mg. of the oxyfluoride was prepared by the various methods, the identity of different samples being established by X-ray powder photographs. *Anal.* Calcd. for Pa_2OF_8: Pa, 73.33; O, 2.54; F, 24.13. Found: Pa, 72.7, 74.0; F, 23.9.

$PaF_5 \cdot 2H_2O$.—The pentafluoride hydrate reported by Grosse[2] was prepared by dissolving Pa_2O_5 in 48% hydrofluoric acid and evaporating the solution to dryness at 110°. A solid mass of colorless, needle-like crystals with a waxy consistency was obtained. Chemical analysis (for Pa and F only) indicated the probable composition $PaF_5 \cdot 2H_2O$. *Anal.* Calcd. for $PaF_5 \cdot 2H_2O$: H, 1.11; Pa, 63.81; F, 26.24; O, 8.84. Found: Pa, 62.5; F, 25.4, 25.7.

The crystals decomposed when heated for several hours at 160° in a current of dry air, leaving a powdery solid which was shown by X-ray analysis to be the oxyfluoride. The formation and decomposition of the dihydrate is indicated by eq. 7 and 8 (gaseous products not analyzed).

$$Pa_2O_5(s) + (nHF, mH_2O) \xrightarrow[25°]{} (\text{solution}) \xrightarrow[110°]{}$$

$$2PaF_5 \cdot 2H_2O(s) + (n - 10)HF(g) + (m + 1)H_2O(g) \quad (7)$$

$$2PaF_5 \cdot 2H_2O(s) \xrightarrow[160°]{} Pa_2OF_8(s) + 2HF(g) + H_2O(g) \quad (8)$$

Analytical Methods.—The pyrohydrolysis apparatus used for fluoride analyses was similar to others described in the literature.[12–14] Steam was generated in a 500-ml. Pyrex flask

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[10] A. J. Walter, Report AERE-M1165, Feb., 1963.

[11] L. Stein, E. Rudzitis, and J. L. Settle, Report ANL-6364, June, 1961.

and passed through a nickel tube, 9 in. long and 3/8 in. in outer diameter, which was heated by a furnace. The weighed sample (5 to 30 mg. of compound) was contained in a small platinum boat near the exit end of the tube. Three distillate fractions were collected in standard NaOH solutions during 30 min. of pyrohydrolysis, and the excess NaOH was back-titrated with standard HCl.

In the pyrohydrolysis of UF_4 and other nonvolatile fluorides, a temperature of 1000° or higher is required. When the first sample of PaF_4 was rapidly pyrohydrolyzed at 1000°, very little oxide was found afterward in the boat. Presumably the volatile oxyfluoride was formed as an intermediate and decomposed downstream in the nickel tube, since the correct amount of HF was recovered. Subsequently the fluoride samples were inserted in the tube at approximately 300°, and the temperature was raised to 700° during the first 10 min. of pyrohydrolysis. Under these conditions, negligible losses occurred, and oxide residues were recovered. It was found that PaF_5, Pa_2OF_8, and $PaF_5 \cdot 2H_2O$ could be pyrohydrolyzed in this manner, as well as PaF_4.

The oxide remaining after pyrohydrolysis was weighed and dissolved in 48% hydrofluoric acid. Several large dilutions were made with 6–12 *M* hydrofluoric acid in polyethylene bottles, using a weight rather than volume basis. Aliquots of solutions were plated on platinum disks by the method of Westrum,[15] and the α activity was then counted and pulse analyzed. After correction for daughter activity, the amount of Pa^{231} was calculated, using a half-life of 34,000 years. (Recent determinations of the half-life of Pa^{231} have yielded values of 32,480 years[16] and 32,800 years.[17] In the present instance, the use of the 34,000 year half-life compensates for the niobium impurity, which reduces the apparent specific activity of the protactinium by 4%.)

Crystallographic Measurements.—X-Ray powder patterns were obtained for all compounds except $PaF_5 \cdot 2H_2O$. Photographs were made with a 9-cm. camera, using copper radiation.

Discussion

Microcrystalline PaF_4 prepared by reaction 1 is dark brown and monoclinic, conforming to the description given previously by Sellers, Fried, Elson, and Zachariasen.[5] The X-ray powder patterns obtained thus far contain only the lines listed in Table I, which are useful for identification but inadequate for determining lattice constants. The tetrafluoride is slightly hygroscopic but does not dissolve readily in water or the following solutions, hot or cold: 48% HF; 2 *M* $NH_4F \cdot HF$; 12 *M* HNO_3; 8 *M* HCl, 0.6 *M* $AlCl_3$; 8 *M* HCl, 1 *M* HF. The addition of H_2O_2 also appears to have little effect on the solubility. The compound can be decomposed and brought into solution by fusion with NaOH and treatment of the resulting cake with 6 *M* HCl. However, analytical results for fluoride are low with such solutions (by PbClF method), probably due to the complexing action of protactinium.

The tetrafluoride is nonvolatile under vacuum up to 800°. When it is heated in a platinum boat inside a quartz tube, considerable decomposition occurs, and both the platinum and quartz are attacked. In nickel apparatus, it appears also to decompose partly at elevated temperatures, but the radioactivity does not move from the initial site.

Table I

PaF_4; Monoclinic (Isostructural with UF_4)

I_0	$\sin^2 \theta$	I_0	$\sin^2 \theta$
m	0.03385	vvw	0.09538
w	0.03861	vvw	0.13235
m	0.04377	w	0.14148
w	0.04618	w	0.15564
w	0.05365	w	0.16416
w	0.08066	vvw	0.17537

Muxart[18] has remarked that the description of PaF_4 given by Haissinsky and Bouissieres[6] differs appreciably from the present description of the anhydrous compound. On reducing Pa(V) in dilute fluoride solution, Haissinsky and Bouissieres obtained a white precipitate, which readily redissolved in dilute hydrofluoric acid after oxidation by air. It is possible that the white material was a hydrated tetrafluoride. However, it seems much more probable from the conditions that an oxyfluoride was formed.

Protactinium pentafluoride is a white, hygroscopic compound, slightly soluble in water, very soluble in 1 *M* or stronger hydrofluoric acid. The crystal lattice is tetragonal ($a_0 = 11.53 \pm 0.01$ Å., $c_0 = 5.19 \pm 0.01$ Å.), isostructural with the β form of UF_5. As previously indicated in tracer experiments,[8] the pentafluoride is much less volatile than VF_5, NbF_5, and TaF_5, but sublimes or distils above 500° at a pressure of 10^{-5} to 10^{-6} mm. It can be handled in prefluorinated nickel or Monel apparatus but reacts with quartz and Pyrex at elevated temperatures.

Volatilization of PaF_5 appears to be useful for the radiochemical purification of protactinium. Samples of the pentafluoride obtained in reaction 2 were shown by α pulse analysis to be almost free of Pa^{231} daughters, whereas the initial PaF_4 in some instances contained 12.3% daughter activity. A 15- to 300-fold reduction in daughter concentration was noted in different experiments. (Half-lives of the daughters are all short in comparison to the half-life of Pa^{231}. Therefore, although daughters contributed significantly to the total radioactivity of most of the compounds, their effect on the chemical purity was entirely negligible.)

From X-ray powder patterns, it was found that Pa_2OF_8 crystallizes in a body-centered cubic lattice ($a_0 = 8.4065 \pm 0.0004$ Å., $Z = 4$), very similar structurally to U_2F_9. The isomorphism is not surprising in view of the nearness in size of protactinium and uranium, oxygen and fluorine. The colors of the two compounds are notably different, however: U_2F_9 is black, due to the resonance of uranium between +4 and higher-valent states[19]; Pa_2OF_8 is white, since protactinium exhibits its normal +5 valence. The molecular structure of the oxyfluoride is not yet known, but very likely two PaF_4 groups are present, linked by oxygen: $F_4PaOPaF_4$.

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The oxyfluoride is hygroscopic, slightly soluble in water, and very soluble in hydrofluoric acid solutions. It is volatile under vacuum above 500° and partly decomposes at 800° and higher temperatures, yielding PaF_5 and other unidentified products (eq. 9). Thus, by

$$Pa_2OF_8(s) \xrightarrow[800°]{} PaF_5(s) + \text{unidentified residue} \quad (9)$$

successive reactions 7, 8, and 9, it is possible to prepare anhydrous PaF_5 from Pa_2O_5 without the use of vigorous fluorinating agents.

Acknowledgment.—The author is indebted to Dr. S. Siegel and Mrs. E. Gebert Sherry for the X-ray analyses and to Mr. D. J. Henderson for the α pulse analyses. He also wishes to express his thanks to Dr. K. W. Bagnall of the Atomic Energy Research Establishment, Harwell, England, for providing initial samples of Pa^{231} and the inducement to undertake the present line of research. The work was begun during a visit to Harwell in 1959 and was later completed at Argonne.

CONTRIBUTION FROM THE GORGAS LABORATORY, ROHM & HAAS COMPANY:
REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALABAMA

The Arsenic Trifluoride-Arsenic Trichloride System

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The species AsF_2Cl and $AsFCl_2$ have been observed in mixtures of $AsCl_3$ and AsF_3 by two independent methods. The formation constants of AsF_2Cl and $AsFCl_2$ have also been determined.

Exchange processes have been observed in phosphorus trihalide systems[1-3] and several mixed phosphorus trihalides have been characterized.[4,5] No examples, however, of mixed arsenic trihalides have been completely characterized, although evidence for such species was found in a study of a mixture of $AsCl_3$ and $AsBr_3$.[3] The Raman spectra of these mixtures contained bands not found in the spectra of the components. These bands were attributed to the exchanged products $AsCl_2Br$ and $AsClBr_2$. Raman spectroscopy, on the other hand, gave no evidence for the existence of AsF_2Cl and $AsFCl_2$[3] in mixtures of arsenic trifluoride and arsenic trichloride. Attempts to prepare these species by partial fluorination of $AsCl_3$ have not been successful either.[6] However, their existence in mixtures of AsF_3 and $AsCl_3$ was demonstrated by using F^{19} n.m.r. and mass spectrometry.

Experimental

Materials.—The arsenic trifluoride and arsenic trichloride used were obtained from commercial sources. Each was purified by distillation in an inert atmosphere. The former was distilled from sodium fluoride. Pyridine (Karl Fischer reagent grade) was used without further purification.

N.m.r. Study.—The F^{19} n.m.r. spectra were obtained with a Varian Model 4300B spectrometer operating at 40 Mc. Chemical shifts were determined with CCl_3F as an internal standard by the side-band technique. The relative areas of the three peaks were obtained by use of an integrating circuit. All solutions were prepared by weight in a nitrogen-filled drybox.

Mass Spectral Study.—The mass cracking patterns were obtained with a Consolidated Systems Corporation high speed mass spectrometer utilizing an ionizing voltage of 70 volts. The gaseous mixtures were prepared in 1–3-ml. calibrated bulb, equipped with Teflon needle valves in the following manners One bulb was filled with a measured pressure of $AsCl_3$ (approximately 10 mm.). This was condensed into a slightly larger bulb with liquid nitrogen. Then the first bulb was filled to the desired pressure with AsF_3. The AsF_3 was then condensed into the bulb containing the $AsCl_3$. The sample bulb was warmed and allowed to age approximately 0.5 hr. Several samples were prepared by allowing known amounts of the gaseous components to mix by diffusion in a closed, greaseless system. No differences in the values for K_1' and K_2' were found between samples prepared by the two methods. The mass cracking pattern of the mixture was obtained by expanding the sample directly into the inlet system (approximately 2 l. in volume). The sensitivities of $AsCl_3$ and AsF_3 were also obtained by this method. The pressure in the inlet system was determined by means of a thermocouple gage.

Mass Spectral Studies

The mass spectrum of a vapor-phase mixture of $AsCl_3$ and AsF_3 contains parent molecule ions for the exchanged species AsF_2Cl and $AsFCl_2$. The assignment of these peaks to the exchanged species was made on the basis of their having the correct m/e ratio and the correct isotopic peaks for chlorine. The fragment ion $AsFCl^+$ at m/e 129 was also obtained from the exchanged species. All other fragment peaks will be obtained both from exchanged and unexchanged species. Only mixtures which contained excess AsF_3 were used due to the relatively low volatility of $AsCl_3$. The mass spectra of a series of mixtures of AsF_3 and $AsCl_3$ were obtained to evaluate the two equilibrium constants necessary to describe the system. The equilibrium constants are defined for the equilibria

$$2AsF_3 + AsCl_3 \underset{}{\overset{K_1}{\rightleftarrows}} 3AsF_2Cl$$

$$2AsCl_3 + AsF_3 \underset{}{\overset{K_2}{\rightleftarrows}} 3AsFCl_2$$

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