HALIDES OF THE ACTINIDE ELEMENTS

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I. Introduction

The binary halides of the actinide elements constitute a most important class of compounds. The actinide elements themselves are, of course, vital to all presently practical means for releasing nuclear energy, and the halides of these elements are leading protagonists in nuclear technology. And, as is the case for other groups of elements in the Periodic Table, the halides are particularly convenient for many kinds of scientific investigations and correlations. Much of what is now known of the electron configuration of the actinide elements, for example, has been learned by experiments with halides. A recapitulation and reassessment of the halides of the actinide elements in the light of recent developments thus becomes appropriate.

The present review will be confined to the solid, binary halides, and principal attention will be focused on developments which have occurred since the subject was last reviewed (*51*). For an interesting and authoritative review of the entire subject of the actinide elements, the recent account of G. T. Seaborg (*74*) can be warmly recommended.

II. Survey of the Actinide Element Halides

The actinide elements now constitute a fairly numerous group of compounds (Table I). An examination of Table I reveals a number of interesting regularities as well as a number of puzzling and unresolved features. It is well known that the actinide elements exhibit a much greater tendency to exist in multiple oxidation states than do the related lanthanide elements. Table II summarizes the known oxidation states of the actinide elements and demonstrates their greater ease of oxidation. It also permits a comparison between the oxidation states of a particular element and its known halides. It is immediately obvious that uranium, neptunium, and plutonium, which possess the greatest tendency to multiplicity in oxidation state, form the largest number of halides. The ability to form higher oxidation states diminishes rapidly in proceeding to elements of higher atomic number; this is reflected in the difficulty in producing higher halides with higher members of the actinide series. In addition to the regularities that are evident, there are also a number of important instances where unexpected discrepancies occur. It may therefore be instructive to examine the situation in detail.

TABLE I

HALIDES OF THE ACTINIDE ELEMENTS[a]

	Ac	Th	Pa	U	Np	Pu	Am	Cm
F	AcF_3			UF_3	NpF_3	PuF_3	AmF_3	CmF_3
		ThF_4	PaF_4	UF_4	NpF_4	PuF_4	AmF_4	CmF_4
				U_4F_{17}		Pu_4F_{17}		
				U_2F_9				
			(PaF_5)	UF_5	$[NpF_5]$	$[PuF_5]$		
				UF_6	NpF_6	PuF_6		
Cl	$AcCl_3$			UCl_3	$NpCl_3$	$PuCl_3$	$AmCl_3$	
		$ThCl_4$	$PaCl_4$	UCl_4	$NpCl_4$			
			$(PaCl_5)$	UCl_5				
				UCl_6				
Br	$AcBr_3$			UBr_3	$NpBr_3$	$PuBr_3$	$AmBr_3$	
		$ThBr_4$	$[PaBr_4]$	UBr_4	$NpBr_4$			
			$[PaBr_5]$					
I	(AcI_3)			UI_3	NpI_3	PuI_3	AmI_3	
		ThI_4	$[PaI_4]$	UI_4				
			$[PaI_5]$					

[a] Parentheses indicate an incompletely characterized compound. Square brackets indicate compounds presumed capable of existence but not as yet prepared.

Little need be said about the halides of actinium. All of the binary halides of this element have been prepared by conventional procedures, and the straightforward, uncomplicated chemical behavior that actinium exhibits generally is also evident here. Thorium, however, presents quite a different problem. Thorium gives no indication of existence in aqueous solution in an oxidation state lower than +4. From considerations of the oxidation potentials it appears quite certain that Th(III) would reduce water strongly, and lower oxidation states of this element appear to be incapable of more than a transitory existence in aqueous media. The situation with respect to possible lower valent solid compounds is more confused, and despite the activity of a number of workers, it is still not possible to give an unequivocal answer to the question of the existence of lower halides of thorium. It appeared from the early work of Warf (*83*) that thorium tetrafluoride is not reduced to ThF_3 on heating with thorium metal at 1175° and 1600°. On the other hand, Anderson and D'Eye (*4*), Hayek *et al.* (*43*, *44*) and Jantsch *et al.* (*48*) all reported the preparation of lower chlorides, bromides, and particularly iodides by thermal decomposition of the appropriate tetrahalide, or by reduction of the tetrahalide with metallic thorium or aluminum at elevated temperatures. Iodides of the composition ThI_3 and ThI_2 were described as dark metallic grey in color with a violet or brownish tinge, and were considered to be analogous to the lower iodides of zirconium that are also described in the literature (*69*, *90*).

TABLE II

OXIDATION STATES OF THE ACTINIDE ELEMENTS[a]

Atomic number	89	90	91	92	93	94	95	96	97	98
Element	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf
Oxidation states	**3**	(3)	(3)	3	3	3	**3**	**3**	**3**	**3**
		4	4	4	4	**4**	(4)	4	4	
			5	5	**5**	5	5			
				6	6	6	6			

[a] The characteristic, stable oxidation state of the element in solution is indicated by boldface type. A doubtful, or unstable, state is enclosed in parentheses.

Watt *et al.* (*84*) have carried out a very careful investigation of the reduction of thorium tetraiodide by metallic thorium. In these experiments, known weights of iodine and thorium, corresponding to different reaction ratios, were mixed and heated at 550° for 3 days. Any tetraiodide present was removed by sublimation, and the nonvolatile residue was separated into a series of fractions by treatment with liquid ammonia, aqueous perchloric acid, and dimethyl formamide. Compositions with a I/Th ratio of 3 dissolved in liquid ammonia with evolution of hydrogen; thorium(IV) amidotriiodide 4-ammoniate, $Th(NH_2)I_3 \cdot 4NH_3$, could be recovered from the liquid ammonia solution. However, in experiments where I/Th ratios varied from 2 to 1, the experiments were interpreted as indicating the presence in the nonvolatile reaction product of ThI_2 and ThI, the first of these insoluble in liquid ammonia but soluble in anhydrous dimethyl formamide, the latter being insoluble in both solvents. Aqueous perchloric acid was employed to separate the lower halides from unreacted thorium metal, because the halides were reported to dissolve in this reagent whereas the metal does not. Despite the care with which the experiments were carried out, several questions remain. The original reaction product is clearly not a pure phase, and inferences based on extraction into dimethyl formamide or perchloric acid do not rigorously establish the formulas of the phases present in the reaction product. Even dilute aqueous perchloric acid has considerable oxidizing power (*46*), and it is not immediately apparent that an aqueous extract with an I/Th ratio of 1 necessarily implies that the original material treated had the composition ThI. Further, Watt and co-workers remark that ThI_3 reduces liquid ammonia readily, but the lower iodides do not; it might be anticipated that ThI_2 and ThI should be even more powerful reducing agents than ThI_3. Young (*90*) found that ZrI_3 dissolved in water to give a solution with transient but strong reducing properties. Similar experiments do not appear to be recorded for ThI_3. Whereas ThI_3 was described by Anderson and D'Eye (*4*) as a volatile substance, and by Hayek *et al.* (*44*) as undergoing disproportionation over the temperature range 500–600°, Watt and co-workers find it to be essentially nonvolatile and stable to disproportionation. Particularly puzzling is the absence of definitive X-ray diffraction data, despite the fact that the preparations are made under conditions which should foster crystal growth. Anderson and D'Eye obtained an X-ray diffraction pattern for ThI_2 and two different patterns for the phase designated ThI_3; the diiodide structure was interpreted in terms of an hexagonal layer-lattice structure similar to other metal diiodides. Hayek *et al.* (*44*) made the somewhat surprising statement that the lower thorium iodides are so sensitive to X-rays as to preclude crystallographic study, while Jantsch *et al.* (*48*) were unable to obtain crystal structure data either by X-ray methods or by electron diffraction. The study of the lower halides of thorium poses a serious experimental problem, necessitating as it does the separation and characterization of solid, nonvolatile mixtures of compounds. An answer might be more readily forthcoming if alternative synthetic procedures that would yield single products could be devised. It is to be hoped that the investigators active in this field will persist in their difficult task in the interest of clarifying the situation.

The gaps in the list of protactinium halides are due not so much to the instability of the missing compounds but rather to difficulties in characterization. Until very recently, protactinium was the least studied of the actinide elements, primarily because of the great difficulties hitherto experienced in obtaining milligram amounts of pure protactinium-231. The lack of pure protactinium and the difficult chemistry of the element have made for slow progress. Nevertheless, sufficient work has been done to show conclusively that halides of both protactinium(IV) and (V) exist as stable, and in the case of the (V) compounds, volatile compounds. The absence of protactinium bromides from Table I therefore can be expected to be soon remedied. The parentheses enclosing $PaCl_5$ in Table I reflect analytical difficulties; the existence of a volatile higher chloride of protactinium appears unequivocal, but as it is not isostructural with the corresponding niobium and tantalum compounds, and in the absence of conventional analytical data, the formula of the volatile higher protactinium chloride is not regarded as fully established.

Uranium possesses the largest and best studied array of halides of any of the actinide elements. Both uranium tetrafluoride and uranium hexafluoride have considerable technological significance. Uranium tetrafluoride is produced on a large scale for the preparation of uranium metal which in turn is used as fuel in nuclear reactors. The tetrafluoride also serves as a starting material for the preparation of uranium hexafluoride. Uranium hexafluoride, by virtue of its high volatility, is used in the thermal diffusion separation of the isotopes U^{235} and U^{238}. Consequently, uranium tetra- and hexafluorides have been studied very intensively. While the situation with respect to physical data is quite satisfactory, the situation regarding chemical behavior is in a much less satisfactory position, and only in the very recent past have chemical studies with UF_6 been taken up. The uranium halides are also unique in the existence of a group of compounds that have been designated "intermediate fluorides." Since discovery of the intermediate fluorides some 15 years ago, little has appeared in the literature. Intermediate in composition between UF_4 and UF_5, the compounds $U_4F_{17}(UF_{4.25})$ and $U_2F_9(UF_{4.50})$ are obtained by reaction of uranium tetrafluoride with uranium hexafluoride (*2*). The existence of these compounds raises the question as to whether similar compounds exist intermediate between UF_5 and UF_6, and whether other actinide elements will form intermediate halides. Mandleberg *et al.* (*58*) have reported the existence of an intermediate fluoride of plutonium which they believe is Pu_4F_{17}. Although not obtained pure, and although X-ray identification is incomplete, it is likely that the compound is indeed an intermediate fluoride. This interesting observation would seem to merit further study.

The neptunium halides illustrate the dictum that higher oxidation states become more difficult to attain for the higher actinide elements. Although on the whole neptunium resembles uranium rather than plutonium, the lower halides of neptunium are distinctly more stable than the corresponding uranium compounds, and distinctly more severe oxidizing conditions are required to prepare NpF_6. Although uranium tetraiodide can be prepared, it is a relatively unstable substance; the corresponding neptunium compound appears to be unstable to the extent that it does not exist under ordinary conditions. Perhaps the most curious feature of the neptunium halides is the absence of a neptunium pentafluoride. Despite a not unconsiderable amount of research, no compound NpF_5 has been characterized, although the (V) oxidation state is ordinarily the most stable neptunium oxidation state in solution. The stability of the neptunium (V) state would thus appear to arise from hydration and oxygenation.

In the case of plutonium, attainment of higher oxidation states is much more difficult than for either uranium or neptunium. It is only in the case of the fluorides that it is possible to prepare other than a tripositive halide. Repeated attempts have been made to prepare plutonium tetrachloride, as for example by subjecting plutonium trichloride to the action of chlorine under high pressure, and it has been concluded that the dissociation pressure of $PuCl_4$ to $PuCl_3$ and chlorine at room temperature must be of the order of several thousand atmospheres. It thus appears unlikely that tetrachlorides or tetrabromides of plutonium will be capable of synthesis. The vacancies in the list of plutonium halides thus occur, not by default, but because of the instability of the higher halides. As in the case of neptunium, no plutonium pentafluoride has been identified. Even though the (V) oxidation state of plutonium is much less stable than is the case for neptunium, it would appear probable that PuF_5 should exist as a stable entity.

The (III) state is by far the most stable oxidation state for americium, and it is possible only by the use of fluorine to prepare a higher halide. Americium tetrafluoride has been prepared by direct fluorination, but attempts to prepare AmF_5 or AmF_6 have so far been fruitless. It is a reasonable presumption that AmF_6 does not exist as a stable compound under ordinary conditions.

Curium resembles americium in the difficulties attendant on preparing higher halides. Here also it would appear that curium tetrafluoride is the highest stable halide, and although no halides other than the fluorides have as yet been prepared, curium trichloride, tribromide, and triiodide should exist. It must be pointed out, however, that curium is an intensely radioactive element. All of the earlier chemical studies were carried out with Cm^{242}, a 162.5-day alpha emitter. Efforts to prepare curium tetrafluoride using this isotope failed, but it was possible to prepare the higher fluoride using one of the longer lived curium isotopes, Cm^{244}, a 19-yr alpha emitter. Presumably Cm^{244}, or an even longer lived isotope such as curium possesses, may be required for the preparation of the other halides of curium.

Table III contains a list of the isotopes of the actinide elements with half-lives for radioactive decay sufficiently long to permit the manipulation of macroscopic quantities. At the present, it does not appear likely that actinide elements above einsteinium will have isotopes sufficiently stable to permit of work on the macro scale.

The isotopes Ac^{227}, Th^{232}, Pa^{231}, and U^{238} occur in nature. The remaining isotopes listed in Table III are purely synthetic. Most of the chemical investigation carried out to date on neptunium, plutonium, americium, and curium have utilized the isotopes Np^{237}, Pu^{239}, Am^{241}, and Cm^{242}. Plutonium, americium, and curium are known, however, to have long-lived isotopes.

TABLE III

ACTINIDE ELEMENT ISOTOPES SUITABLE FOR INVESTIGATIONS WITH MACROSCOPIC QUANTITIES

Element	Isotope	Half-life	Alpha disintegration per minute per milligram
Actinium	Ac^{227}	22.0 yr	1.59×10^{11}
Thorium	Th^{232}	1.39×10^{10} yr	2.47×10^{2}
Protactinium	Pa^{231}	34,300 yr	1.00×10^{8}
Uranium	U^{238}	4.50×10^{9} yr	7.42×10^{2}
Neptunium	Np^{237}	2.20×10^{6} yr	1.52×10^{6}
Plutonium	Pu^{239}	24,360 yr	1.36×10^{8}
	Pu^{242}	3.79×10^{5} yr	8.66×10^{6}
	Pu^{244}	7.6×10^{7} yr	4.29×10^{4}
Americium	Am^{241}	458 yr	7.19×10^{9}
	Am^{243}	7,600 yr	4.29×10^{8}
Curium	Cm^{242}	162.5 day	7.38×10^{12}
	Cm^{244}	19 yr	1.72×10^{11}
	Cm^{247}	$\geq 4 \times 10^{7}$ yr	$<8.04 \times 10^{4}$
	Cm^{248}	4.7×10^{5} yr	6.79×10^{6}
Berkelium	Bk^{247}	7×10^{3} yr	4.60×10^{8}
	Bk^{249}	314 day	3.71×10^{12}
Californium	Cf^{249}	360 yr	8.86×10^{9}
	Cf^{251}	660 yr	4.80×10^{9}
Einsteinium	E^{254}	280 day	4.07×10^{12}

When these isotopes become available, chemical studies will be greatly simplified, and the complications introduced by the radioactivity of the actinide elements will be substantially minimized. The longest-lived isotopes of berkelium, californium, and einsteinium are still fairly short-lived substances, and macroscopic amounts have a tremendous associated radioactivity. Nevertheless, it should eventually be possible to prepare and study the solid halides of the actinide elements through the element einsteinium using weighable amounts of reactants. This remains for the future, however. The special experimental problems associated with highly radioactive substances are considered below.

III. Preparative

A. GENERAL CONSIDERATIONS

While the reactions employed in the synthesis of the actinide element halides are for the most part quite conventional, the actual experimental procedures are unusual and distinctive. This circumstance arises from the radioactivity of the actinide elements, and the chemical and physiological consequences which ensue. Referring to Table III, it can be seen that the emission of alpha particles by the shorter-lived actinide isotopes is prodigious. Alpha particles do not usually pose an external radiation threat, but ingestion is quite another matter. For example, Pu^{239} inhaled into the lungs is to a considerable extent transferred to and deposited in the skeleton. Long continued alpha emission in the bone in a localized region may result in the development of bone cancer, and for the human about one microgram of Pu^{239} fixed in the skeleton is considered a potentially lethal dose (*55*). While all of the actinide elements are not metabolized in the same way, nevertheless, all except uranium are easily fixed in the skeleton, and all present an ingestion hazard. Means have therefore been devised to minimize contact between the investigator and his experimental material. Figure 1 shows an arrangement frequently used for the manipulation of intense alpha-emitting isotopes. Essentially a ventilated hood (fume cupboard) for radiochemical research, it is converted for use with alpha-emitters by the insertion of a glove panel. This seals the hood, and provides a set of gloves through which experimentation is carried out. A plastic port for introducing and removing apparatus and samples from the hood is is also provided. When the hood must be opened, air is drawn from the face of the hood through the set of air filters shown in the back of the hood to keep contaminants from leaving the hood. The particular hood illustrated is equipped for the manipulation of plutonium and fluorine. Another piece of apparatus that finds extensive use is shown in Fig. 2. This is a ventilated vacuum frame. Many of the preparations of actinide halides are carried out by vacuum line manipulation, and often the vacuum line is too large to fit into a gloved-box. The entire vacuum line can be placed in the enclosure shown and very large amounts of air can be moved past the apparatus. The door slides and the entire container may be closed, or any particular panel may be moved to allow access to a portion of the apparatus. In case of accident, the ventilation provisions are adequate to prevent material from entering the room. Most of the experimental work with the extremely hazardous plutonium hexafluoride has been carried out in such an enclosed vacuum line. Bagnall (*8*) gives a very useful description of laboratory techniques applicable in many cases to work with actinide compounds.

Micro techniques have been very useful in chemical studies of the actinide elements, and particularly so for the study of the halides. Historically, micro methods were required because of the very small amounts of the synthetic actinides originally available for experiment. However, even when large amounts of neptunium, plutonium, and other actinide elements became available, micro methods were found to offer many advantages, and they have therefore continued to be of great service to this day. W. H. Zachariasen was able to obtain and interpret X-ray diffraction patterns on samples of the order of a few micrograms and the results obtained in this way have been of the greatest utility in the identification of new compounds. The hazards attendant on the preparation of compounds of such short-lived isotopes as Ac^{227} or Cm^{242} are greatly decreased by such techniques because such very small amounts are used. In the case of Ac^{227}, which generates a host of beta- and gamma-emitting daughters by radioactive decay, it is a necessity and not a convenience to employ microgram amounts. When large amounts of Ac^{227} are used, conventional X-ray diffraction methods are no longer applicable, as the beta and gamma background produced by the daughter activities fogs the X-ray film. While special methods can be employed to obtain X-ray diffraction

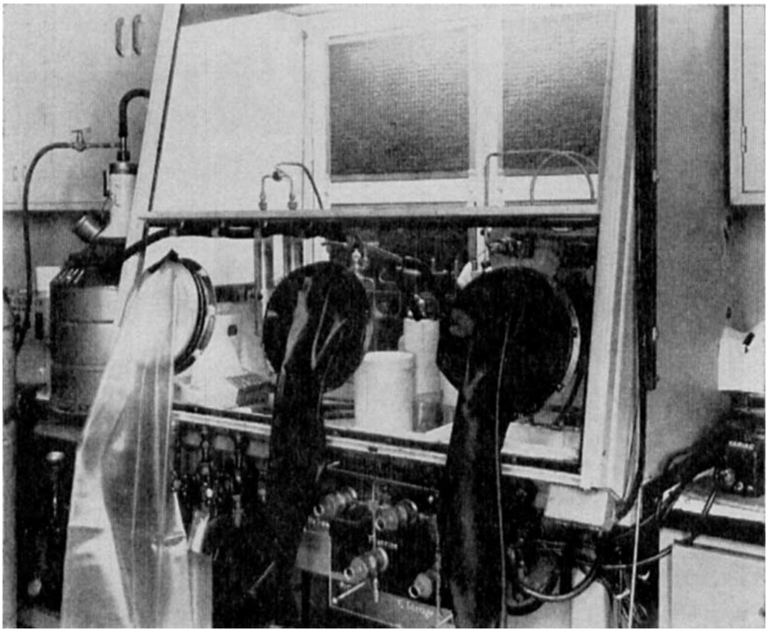

FIG. 1. Ventilated hood for radiochemical manipulation.

data in the presence of a considerable gamma background, nevertheless, it is much more convenient to resort to micro methods.

Capillary techniques can be successfully used in the range of a few micrograms to perhaps a milligram of sample. The essence of the capillary technique is to use the X-ray capillary as the reaction vessel. The preparative and purification procedures are carried out in the capillary tube used to secure the X-ray diffraction pattern, thus avoiding losses in transfer and possible exposure of the sample to air or moisture. The application of capillary techniques to the synthesis of actinide element compounds has been described by Fried and Davidson (*34*) and Sheft and Fried (*76*). For many purposes, experimentation on about the milligram scale appears to be optimum in scale. This is particularly true for work with neptunium and

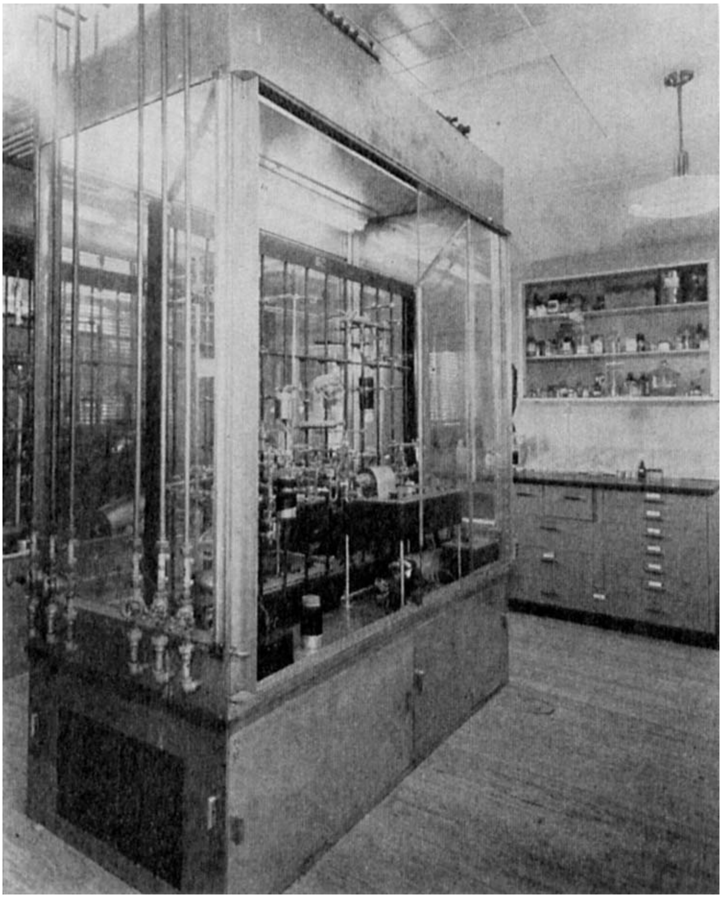

FIG. 2. Ventilated vacuum frame hood.

plutonium, and much of the chemistry of the solid compounds of these elements has been learned from work on the milligram scale. More conventional chemical procedures may be employed on the milligram scale but here also X-ray methods are basic.

As might be expected, the bulk of the research activities relating to halides of the actinide elements has concerned itself with compounds important in nuclear technology. The preparation and properties of UF_4, UF_6, and PuF_6 have consequently received much attention. Another reason for the interest in fluorides is the ability of fluorine to evoke highest oxidation states. The actinide elements themselves have not all attracted the same amount of study; thus, nothing has appeared in the literature on actinium since the pioneering study of Fried *et al.* (*36*). The same is true for the protactinium halides where nothing appears in the literature subsequent to the original communication of Sellers *et al.* (*75*). Presumably this situation is a consequence of the great difficulty in obtaining pure protactinium, and it is reasonable to assume that the paucity of information on the protactinium halides will soon be rectified because of the success of Maddock and co-workers in isolating large amounts of pure protactinium (*40*).

B. LOWER FLUORIDES

The lower fluorides of the actinide elements are prepared by reaction with hydrogen fluoride, either in aqueous solution or at elevated temperatures in the dry way. The latter is the more usual procedure. The methods used for the preparation of UF_4 are typical of those used for the preparation of the lower fluorides of any of the actinide elements. The usual starting material for the preparation of uranium tetrafluoride is the trioxide, UO_3, obtained by thermal decomposition of uranyl nitrate hexahydrate, $UO_2(NO_3)_2 \cdot 6H_2O$. The trioxide is reduced by hydrogen to uranium dioxide, which is in turn hydrofluorinated to UF_4:

$$UO_3 + H_2 \rightarrow UO_2 + H_2O,$$

$$UO_2 + 4HF \rightarrow UF_4 + 2H_2O.$$

For the other actinide elements the usual starting material will be the dioxide. Although these reactions appear to be simple, they are in fact quite complex. Uranium trioxide as prepared by thermal decomposition of uranyl nitrate hexahydrate, uranium peroxide, or ammonium diuranate may exist in any one of at least four crystal modifications and in an important amorphous form. The reduction of UO_3 appears to be related both to the crystal form and to the surface area, and depending on these and perhaps other still unspecified variables, the hydrofluorination reaction on the uranium dioxide so obtained may proceed smoothly to essentially complete reaction, or only very slowly and incompletely. Kuhlman and Swinehart (*52*) have reported a detailed study of the factors involved in obtaining quantitative hydrofluorination of UO_2. The rate of hydrofluorination of a given sample of uranium dioxide depends upon the temperature at which it has been prepared (Fig. 3). If UO_3 is reduced at a temperature above 650°, appreciable sintering occurs, and the dioxide obtained is of low surface area and low reactivity. A number of competing processes also are involved in the hydrofluorination reaction. Although the rate of the reaction increases with temperature, should sintering occur, the rate of hydrofluorination may appear to decrease with temperature. The initial hydrofluorination reaction is very rapid even at 400°, and local temperatures may be attained considerably in excess of the nominal temperature because of the heat of reaction. The more reactive the original starting material, the greater is the likelihood of incomplete reaction because of sintering. Another complicating factor is the reversibility of the hydrofluorination reaction; the reactants and products will come to an equilibrium determined by the flow characteristics of the reaction system. The value of the equilibrium constant of the hydrofluorination reaction is in doubt, and values for K_p, where $K_p = p_{H_2O}{}^2/p_{HF}{}^4$($p_{H_2O}$ and p_{HF} are equilibrium pressures in atmospheres) ranging from 30 to 400 have been reported (*79*). A rapid flow of hydrogen fluoride is thus desirable in order to displace the equilibrium in the desired direction. The problem of sintering is merely troublesome on

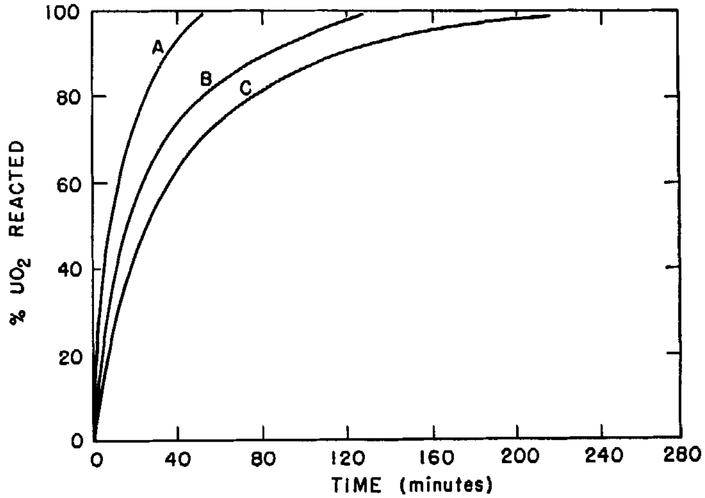

FIG. 3. Rate of hydrofluorination of uranium dioxide samples at 575° (*52*). Sample *A*, UO_3 reduced at 450°; *B*, at 540°; *C*, at 780°.

the laboratory scale, but it can make the difference between success and failure on the large scale. Consequently, fluidized bed processes have been developed that considerably minimize these difficulties (*49*).

Hydrogen fluoride is not the only reagent that can be used for the high-temperature dry-way preparation of uranium tetrafluoride. Cacciari *et al.* (*14*) have described the preparation of uranium and thorium tetrafluorides by the reaction at 400° of uranium trioxide or thorium dioxide with fluorinated hydrocarbons:

$$UO_3 + 2CF_2Cl_2 \rightarrow UF_4 + CO_2 + COCl_2 + Cl_2,$$

$$ThO_2 + 2CF_2Cl_2 \rightarrow ThF_4 + 2COCl_2.$$

The reagent CF_2Cl_2 (Freon-12) was first introduced for this purpose by Booth *et al.* (*11*) and has the considerable advantage that, unlike hydrogen fluoride, it can be used in quartz apparatus.

Because hydrates of uranium tetrafluoride, as well as the hydrates of lower fluorides of the actinide elements, generally undergo extensive hydrolysis when attempts are made to dehydrate them, preparative methods involving aqueous solutions have fallen into disuse. If fluoride ion is added to an aqueous solution of U^{4+}, hydrated $UF_4 \cdot 2.5\ H_2O$ is obtained. This hydrate can readily be dehydrated to the monohydrate $UF_4 \cdot H_2O$, but the removal of the last molecule of water is a matter of some difficulty. Nevertheless, aqueous methods appear to be having a new vogue, presumably because of the advantages inherent in carrying out the preparation in aqueous solution at moderate temperatures. Allen *et al.* (*3*) have described the preparation of uranium tetrafluoride from aqueous solutions of uranyl ion, UO_2^{++}. Tin(II)chloride, copper(I)chloride, chromium(II)chloride, and titanium(III)chloride are all effective agents for the reduction of UO_2^{++} to U^{4+}. However, a catalytic reduction process in which sulphur dioxide is used as the reducing agent was found to be especially useful. While SO_2 does not ordinarily reduce UO_2^{++}, reduction is rapid in the presence of catalytic quantities of copper ion. Sulphur dioxide presumably reduces Cu^{++} to Cu^{+}, and this species is known to reduce UO_2^{++}. Hydrofluoric acid is added to the uranyl solution, and the reduction and precipitation are carried out with SO_2 in the presence of a small amount of copper ion. The reaction is carried out at 85–95° and the product obtained is $UF_4 \cdot 0.75\ H_2O$. This can be dehydrated to anhydrous UF_4 by heating in a hydrogen fluoride gas stream. An interesting variant is the use of electrolytic reduction for the wet-way preparations of uranium tetrafluoride (*72*). The dehydration of thorium tetrafluoride has also received study. D'Eye and Booth (*20, 21*) have studied the precipitation of thorium tetrafluoride from aqueous solution. Three hydrates have been described: $ThF_4 \cdot 2.5\text{–}3.0\ H_2O$ ($ThF_4 \cdot xH_2O$, pseudo-tetragonal), $ThF_4 \cdot 0.5\text{–}2.0\ H_2O$, ($ThF_4 \cdot yH_2O$, orthorhombic), and a hydrate of probable composition $ThF_4 \cdot 0.25\ H_2O$ ($ThF_4 \cdot zH_2O$). The first two hydrates were prepared by adding a slight excess of hydrofluoric acid to a Th^{4+} solution, and the phase $ThF_4 \cdot zH_2O$ was prepared by the thermal degradation of the higher hydrates. $ThF_4 \cdot xH_2O$ is obtained when the precipitate is separated from the mother liquor immediately after precipitation, whereas $ThF_4 \cdot yH_2O$ is formed when the hydrated precipitate is allowed to remain in contact with the mother liquor for 48 hr. Removal of water at 300° in air or vacuum gave a product of composition $ThF_4 \cdot 0.1-0.2\ H_2O$ (phase 2) different from that of monoclinic ThF_4 (phase 1). Phase 1 could be obtained from phase 2 by heating in vacuum at 400°. The complex relations existing in this superficially simple system are shown in Fig. 4.

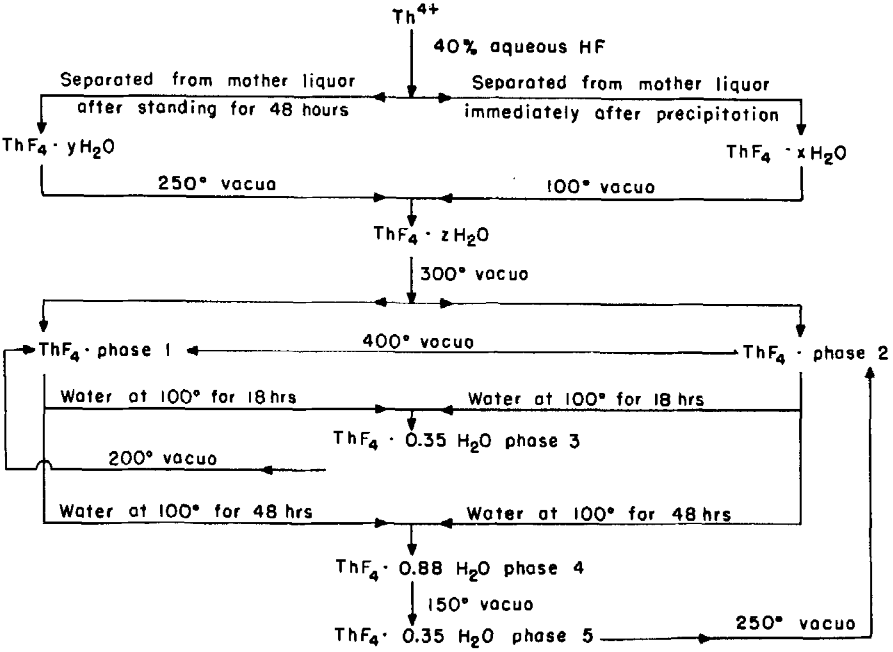

FIG. 4. Preparation of the hydrates of thorium tetrafluoride (*21*).

It is on occasion necessary to prepare uranium tetrafluoride from uranium hexafluoride, particularly when dealing with material highly enriched in U^{235}. The conversion of uranium hexafluoride to the tetrafluoride has has therefore attracted considerable study, and the present situation is summarized by Smiley and Brater (*80*). Uranium hexafluoride can be reduced with hydrogen. The thermodynamic equilibrium, even at room temperature, is in favor of the formation of uranium tetrafluoride, but the reaction requires a high energy of activation to inaugurate reduction. The heat required to initiate the reaction can be supplied either by the reactor walls or by the highly exothermic reaction of hydrogen with a small amount of elemental fluorine which is added to the uranium hexafluoride. Trichloroethylene can also be utilized as a reducing agent, but the product uranium tetrafluoride may be contaminated with organic by-products.

The transuranium element lower fluorides can be prepared by quite analogous procedures. Westrum and Eyring (*88*) have described a platinum hydrofluorination apparatus (Fig. 5) that is very useful on the microgram or milligram scale, and has been used for the preparation of americium trifluoride by the hydrofluorination of Am_2O_3 with anhydrous hydrogen fluoride at 650°. The trifluorides of the actinide elements (where they are stable) can be prepared in a variety of ways. Uranium trifluoride is best obtained by reduction of the tetrafluoride, and aluminum is the most convenient reagent for this purpose(*70*):

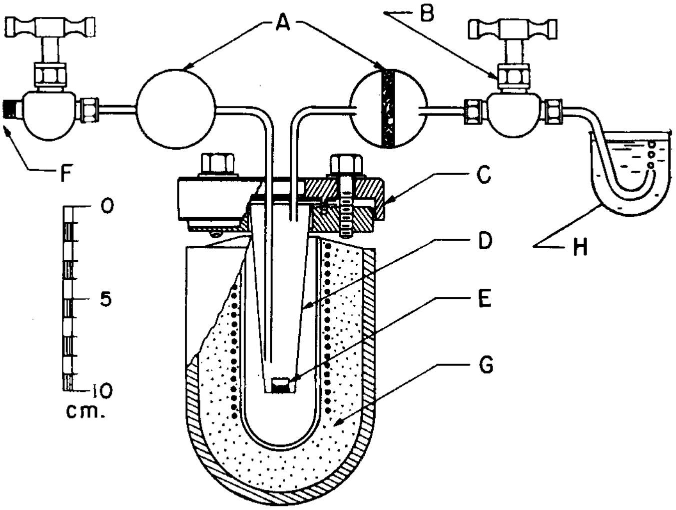

FIG. 5. Platinum hydrofluorination apparatus (*88*). *A*, platinum spheres with filter disks of sintered platinum; *B*, brass needle valves; *C*, stainless steel block clamps; *D*, platinum reactor; *E*, platinum vessel; *F*, to manifold; *G*, furnace; *H*, plastic bubbler with fluorocarbon oil.

$$UF_4 + Al \xrightarrow{900°C} UF_3 + AlF \nearrow.$$

A procedure of this kind is practically obligatory for the preparation of UF_3 because the uranium(III) oxidation state is only barely stable in aqueous solution; attempts to precipitate solid compounds from a U^{3+} solution invariably yield compounds of uranium(IV). For the transuranium elements, however, either aqueous or high-temperature dry-way procedures may be employed. Plutonium trifluoride is insoluble in water and may therefore be prepared by precipitation from aqueous solution by addition of hydrofluoric acid to a Pu^{3+} solution. Anhydrous PuF_3 can be obtained from the hydrated trifluoride by heating in a stream of hydrogen fluoride at 200–300°. Addition of F^- ion to a solution of plutonium(IV) forms $PuF_4 \cdot 2.5\ H_2O$, analogous to $UF_4 \cdot 2.5\ H_2O$ obtained under comparable conditions. Attempts to dehydrate $PuF_4 \cdot 2.5\ H_2O$ yield PuF_3 and not the expected PuF_4. Dawson *et al.* (*19*) account for this state of affairs by the reaction scheme:

$$\begin{array}{c} PuF_4 + 2H_2O \rightleftarrows PuO_2 + 4HF \\ 3PuF_4 + PuO_2 \rightleftarrows 4PuF_3 + O_2 \\ \hline 4PuF_4 + 2H_2O \rightleftarrows 4PuF_3 + 4HF + O_2 \end{array}$$

This behavior is clearly consistent with the increasing stability of the lower oxidation states as one proceeds to actinide elements of higher atomic number.

Both plutonium trifluoride and tetrafluoride can be prepared by hydrofluorination of plutonium dioxide. The oxidation-reduction relations of plutonium(III) and (IV) are such that it is readily possible to specify which of the fluorides shall be the product. If the reaction is carried out under reducing conditions, then the product is PuF_3, and under oxidizing conditions, PuF_4:

$$PuO_2 + 3HF + \tfrac{1}{2}H_2 \xrightarrow{600°C} PuF_3 + 2H_2O,$$

$$PuO_2 + 4HF + O_2 \xrightarrow{550°C} PuF_4 + 2H_2O + O_2.$$

Cylinders of hydrogen fluoride stored for any length of time contain hydrogen gas formed by reaction with the iron container. Hydrogen fluoride drawn from such a cylinder will yield only PuF_3 because of the reducing atmosphere provided by the hydrogen. To obtain PuF_4, oxygen may be added to assure the absence of reducing agents; under these conditions PuF_4 is the sole product. Similar considerations apply to NpF_3 and NpF_4.

Of the transplutonium elements, one of the most interesting results obtained in recent years relates to the preparation of curium tetrafluoride. The (III) oxidation state is the characteristic one for curium, and curium trifluoride is readily prepared by precipitation from aqueous solution (*27*). Attempts to prepare curium tetrafluoride by fluorination of the trifluoride, analogous to the successful preparation of americium tetrafluoride from the trifluoride, were uniformly unsuccessful as long as the short-lived isotope Cm^{242} (162.5-day alpha-emitter) was used. Asprey *et al.* (*7*) were able to convert CmF_3 to CmF_4 with elemental fluorine at 400°, provided Cm^{244}, an alpha-emitter of 18.4-yr half-life was used. Presumably the longer-lived isotope causes less radiation damage to the compound. Curium tetrafluoride is monoclinic, and is isostructural with uranium tetrafluoride and the other actinide element tetrafluorides.

C. Higher Fluorides

The higher fluorides of the actinide elements are certainly among the most interesting of the actinide halides. The volatility of the MF_6 compounds makes them of great practical interest, and the unique opportunity to study a rare-earthlike electron configuration in the gaseous state makes the triad UF_6, NpF_6, and PuF_6 of equally great scientific interest. Considerable information on these compounds has been obtained in recent years, mainly by Weinstock and co-workers, and this area of research has seen perhaps the most interesting and significant work in the entire area of actinide halide research in recent years.

Uranium hexafluoride is prepared industrially on a very large scale for uranium isotope separations. All compounds of uranium, including of course the metal, react with fluorine to yield the hexafluoride if the reaction is allowed to proceed under sufficiently vigorous conditions. In general, UF_6 is prepared by the fluorination of uranium tetrafluoride, this being the procedure that requires the least amount of the expensive reagent, fluorine:

$$UO_3 + 3F_2 \rightarrow UF_6 + \tfrac{3}{2}O_2,$$

$$U_3O_8 + 9F_2 \rightarrow 3UF_6 + 4O_2,$$

$$UO_2 + 3F_2 \rightarrow UF_6 + O_2,$$

$$UF_4 + F_2 \rightarrow UF_6.$$

The fluorine content of UF_4 is derived from the relatively inexpensive reagent, hydrogen fluoride, so that only two of the six fluorine atoms of UF_6 are obtained from elemental fluorine. Brater and Smiley (*12*) have given an excellent description of the laboratory scale preparation of UF_6 by the UF_4-F_2 reaction.

Labaton and Johnson (*53*) have made a kinetic study of the fluorination of uranium tetrafluoride by fluorine. The reaction was studied in the temperature range 265–348° by following the change in weight of the solid phase with a copper-beryllium spring balance. No detectable reaction is noted at 220°, but the reaction rate is measurable at 230°. The rate at which UF_6 is produced is in agreement with the kinetics expected for the reaction between a gas at a spherical interface that is continuously being reduced due to reaction with the gas. The rate law can be expressed by the equation of Anderson (*5*) for the case of a gas-solid reaction governed by a diminishing interface. From the temperature variation of the rate, an activation energy of 19.1 kcal/mole, for UF_4 prepared by hydrofluorination, is deduced. The mechanism of the reaction can be visualized in the following terms: Formation of uranium hexafluoride proceeds by adsorption of fluorine on the surface of the uranium tetrafluoride particles. The fluorine migrates into the crystal lattice with the formation of a "nonstoichiometric" intermediate compound of variable composition richest in fluorine near the surface. Uranium hexafluoride is continuously evolved from the surface as long as the partial pressure of uranium hexafluoride in the system is less than the dissociation pressure of the intermediate to form UF_6. The particles of uranium tetrafluoride diminish in size as the reaction proceeds. The migration of fluoride ions into the uranium tetrafluoride lattice is conceived as an essential feature of the mechanism. Apart from the possible impropriety of designating the intermediate fluorides participating in the reactor as nonstoichiometric compounds, the suggested mechanism appears to be a reasonable one.

Elemental fluorine is not the only reagent that can be used for the fluorination of uranium tetrafluoride. The halogen fluorides were first used for the preparation of actinide fluorides by Emeléus *et al.* (*25, 26*). Particularly useful are chlorine trifluoride and bromine trifluoride. The former is usually used as a gas because of its low boiling point of 12°, whereas bromine trifluoride boiling at 126° can be used as a liquid phase reagent. Both of these reagents have been employed in the processing of uranium fuels from nuclear reactors; the irradiated uranium, fission products, and plutonium are converted to fluorides, and are separated by taking advantage of differences in volatility. The uranium is recovered as uranium hexafluoride and is obtained in a very high degree of both chemical and radiochemical purity by fractional distillation (*9, 47*). Labaton (*54*) has reported a kinetic study of the fluorination of uranium tetrafluoride by gaseous chlorine trifluoride. The mechanism of the reaction, according to Labaton, is essentially the same for chlorine trifluoride as for fluorine. The reaction rate passes through a maximum at 105°, falls to a minimum at 148° and then rises again. The lower reaction rate constants in the temperature interval are attributed to the lower rate at which chlorine trifluoride reacts with the surface intermediate fluoride as compared to uranium tetrafluoride; above 150°, intermediate fluorides do not form and the rate of hexafluoride formation rises again. The activation energy is much lower and the reaction proceeds at consideraly lower temperatures than is the case when elemental fluorine is used. The halogen fluorides thus appear to have definite advantages in the preparation of uranium hexafluoride. The phase diagrams for the uranium hexafluoride-chloride trifluoride and uranium hexafluoride-bromine pentafluoride have been studied (*23*). The uranium hexafluoride-chlorine trifluoride system shows complete miscibility in the liquid phase at 67° but partial miscibility at 75° over a limited composition range; no azeotropes exist in this system. The uranium hexafluoride-bromine pentafluoride system exhibits complete miscibility over the range 68–80°, and has a single maximum vapor pressure azeotrope at a composition of approximately 0.1 mole fraction of uranium hexafluoride. The uranium hexafluoride-bromine trifluoride system has also been investigated (*30*); the system is of the simple eutectic type and exhibits positive deviations from ideality.

Whether elemental fluorine or one of the halogen fluorides is employed, preparation of uranium hexafluoride by fluorination requires the preparation of elemental fluorine, because the preparation of the halogen fluorides require elemental fluorine. Fried and Davidson (*33*, *37*) discovered, however, that it is possible to obtain uranium hexafluoride by the reaction of uranium tetrafluoride with dry oxygen at 800° according to the reaction

$$2UF_4 + O_2 \rightarrow UF_6 + UO_2F_2.$$

The reaction can be made the basis for a cyclic process for the preparation of uranium hexafluoride without the use of elemental fluorine:

$$\begin{aligned} 2UF_4 + O_2 &\rightarrow UF_6 + UO_2F_2 \\ UO_2F_2 + H_2 &\rightarrow UO_2 + 2HF \\ UO_2 + 4HF &\rightarrow 2H_2O + UF_4 \end{aligned}$$

The fluorine content thus is obtained entirely from low-cost hydrogen fluoride. This reaction, because of its potential large-scale utility, has therefore been the subject of a number of investigations. Ferris (*28*) has examined the side reactions and thermodynamics of the oxidation in the temperature range 600–900°. In addition to the expected products UF_6 and UO_2F_2, Ferris observed the formation of uranium pentafluoride. Its formation was postulated to be the result of a side reaction between UF_6 and UF_4. Detailed experiments indicated also that the reaction

$$3UF_4 + O_2 \rightarrow 2UF_5 + UO_2F_2$$

makes a significant contribution to the observed stoichiometry at elevated temperatures. In the temperature range studied, only slight decomposition of uranyl fluoride was noted, in accordance with thermodynamic predictions. In a subsequent publication, Ferris (*29*) has examined the kinetics of the uranium tetrafluoride-oxygen reaction by a thermogravimetric method in the temperature range 550–815°. The reaction shows a first-order dependence on the surface area of the uranium tetrafluoride; the rate is also dependent on the oxygen partial pressure. The rate for the reaction with dry oxygen can be expressed as $k = 8.31 \times 10^6 \exp(-45{,}900/RT)$, where k has the units of moles per minute per square meter.

As usually prepared, uranium hexafluoride may be contaminated with other volatile fluorides, and hydrogen fluoride, molybdenum hexafluoride, vanadium oxyfluoride are among the common and objectionable impurities that may be present. Purification is usually achieved by distillation procedures and a considerable amount of useful and practical information on purification procedures has recently become available (*24*, *62*, *81*). A procedure for the purification of UF_6 that has been recently introduced by Cathers *et al.* (*15*) involves the formation of a complex compound between uranium hexafluoride and an alkali metal fluoride. Ruff and Heinzelmann (*68*) first observed complex formation between uranium hexafluoride and sodium or potassium fluoride, and this was confirmed by Martin *et al.* (*59*). These reports were received with a certain reserve, because efforts made during World War II to prepare addition compounds of uranium hexafluoride were singularly unsuccessful (*41*). Nevertheless, complex compounds are indeed formed, according to the reaction

$$UF_6 + 3NaF \rightleftarrows Na_3UF_9.$$

The reaction is reversible, and uranium hexafluoride is evolved on heating; it is this factor that makes the addition compound useful for the recovery or purification of uranium hexafluoride. The dissociation pressure of the complex compound in the temperature range 80–320° is given by the equation $\log p = 10.88 - (5.09 \times 10^3/T)$, where p is the partial pressure of UF_6 in millimeters of mercury, and T is the absolute temperature. A decomposition pressure of 1 atm is calculated to occur at 363°, and an enthalpy of formation of -23.2 kcal/mole of UF_6 is deduced for the formation of the complex. The kinetics of the reaction between uranium hexafluoride and sodium fluoride have been studied by Massoth and Hensel (*60*, *61*). The reaction appears to proceed initially at a rate determined by the surface area of the sodium fluoride, and then to become diffusion limited. The rate of the reaction is given by the expression $k = 5.0 \times 10^6 \exp(-13{,}000/RT)$ per hour; the activation energy is thus 13.1 ± 0.2 kcal/mole of uranium hexafluoride.

A study of the uranium hexafluoride–metal fluoride complexes was undertaken by Sheft *et al.* (*77*) by the use of radioactive fluorine-18 exchange methods. The exchangeability of fluorine between uranium hexafluoride and metal fluorides can be used as a measure of the extent to which reaction occurs. If a complex compound actually forms between uranium hexafluoride and a metal fluoride, then the fluorine atoms become equivalent and randomization of the radioactivity occurs. Complete exchange of the fluorine atoms is found to occur between sodium fluoride labeled with F^{18} and uranium hexafluoride. The data are consistent with the formation of $UF_6 \cdot 2NaF$ rather than $UF_6 \cdot 3NaF$; the exchange results may be interpreted on this basis or that the complex $UF_6 \cdot 3NaF$ does form, but that only three of the six fluorine atoms originally in the UF_6 are capable of exchange with sodium fluoride. The former alternative seems the more likely. At a temperature of 350°, where the uranium hexafluoride–sodium fluoride addition compound is essentially completely dissociated, no exchange of fluorine is observed to occur. The evidence for the formation of a true complex between sodium fluoride and uranium hexafluoride thus appears quite good. No exchange was observed to occur between uranium hexafluoride and lithium fluoride, potassium fluoride, silver fluoride, and zirconium tetrafluoride labeled with F^{18}. The ability to form an additive compound with uranium hexafluoride thus appears to be limited to sodium fluoride of the metal fluorides tested. Since the X-ray diffraction pattern of the sodium fluoride complex has not as yet been interpreted, a geometrical reason for the observed specificity, although probable, remains to be established.

Neptunium hexafluoride was first prepared by A. E. Florin and has recently been studied in detail by Weinstock and his collaborators. Neptunium hexafluoride can be prepared by the fluorination of NpF_3 or NpF_4 at 500°. Since neptunium hexafluoride requires a rather higher temperature of formation and is less stable than uranium hexafluoride, an ingenious apparatus that enables the reaction to proceed at elevated temperatures and still allows the product to be rapidly cooled is employed (Fig. 6) (*57*). Liquid fluorine drips from the liquid-nitrogen cooled condenser onto the heated starting material, NpF_3 or NpF_4. A high local concentration of fluorine is thus maintained in the reaction zone; convection currents carry the product NpF_6 to the condenser where it is trapped. Neptunium hexafluoride is bright orange in color, unlike colorless uranium hexafluoride, and appears to be susceptible to photodecomposition.

Although the existence of a volatile higher fluoride of plutonium had been surmised from tracer experiments, positive evidence of the existence of PuF_6 was obtained by Florin (*31*) who first prepared the compound. An investigation of the preparation and properties of PuF_6 was also conducted by Mandleberg *et al.* (*58*), but in recent years the compound has been most intensively studied by Weinstock and his collaborators. Plutonium hexafluoride can be prepared by a variety of procedures similar to those used for the preparation of uranium hexafluoride. The most widely used method consists in the fluorination of plutonium tetrafluoride with elemental fluorine. Whereas uranium hexafluoride can be prepared by the analogous reaction at 300°, and neptunium hexafluoride at 500°, the preparation of plutonium hexafluoride by this reaction appears to require a temperature of 750° in order to achieve useful rates of reaction. Since plutonium hexafluoride is alleged to be thermally unstable, it is essential that the freshly formed plutonium hexafluoride be rapidly chilled to a temperature where the rate of decomposition is slow. Weinstock and Malm (*85*) have described a reactor for simultaneously carrying out the preparation at a high temperature and at the same time providing a low-temperature condenser (Fig. 7). The starting charge of plutonium tetrafluoride is placed in a nickel crucible which is inserted into the coil of an induction heater. Fluorine is then introduced into the reaction vessel. The coil, which is of copper tubing, is cooled by the circulation of liquid nitrogen and thus serves the dual purpose of heating the plutonium tetrafluoride and simul-

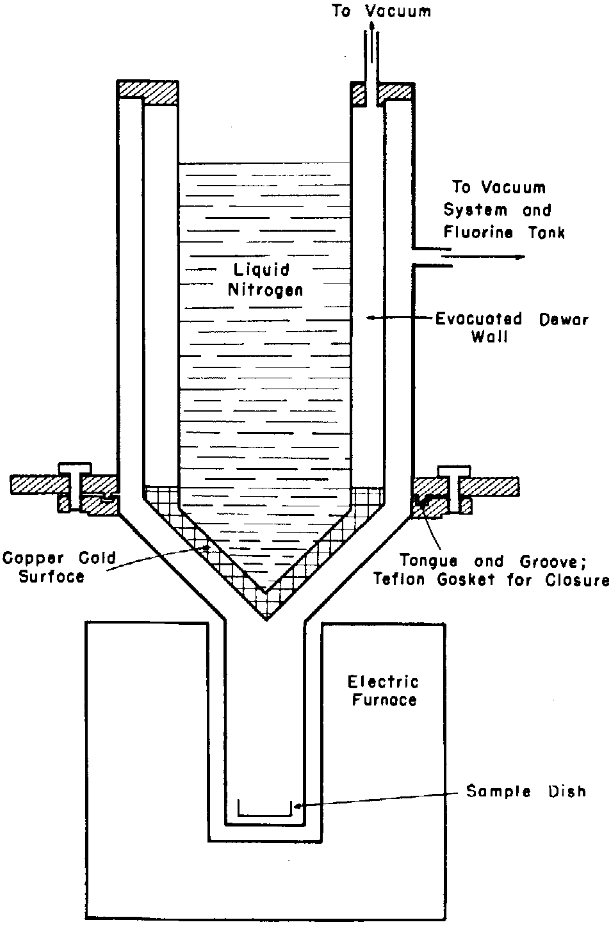

FIG. 6. Reactor for neptunium hexafluoride (*57*).

taneously providing a condenser. Gram amounts of plutonium hexafluoride have been prepared in this reactor. The fluorination of plutonium tetrafluoride by elemental fluorine has been studied in a flow system in the temperature range between 100° and 600°. Activation energies between 10 and 12 kcal/mole were obtained. In contrast to earlier workers, Steindler *et al.* (*82*) and Adams *et al.* (*1*) found that plutonium tetrafluoride can be fluorinated to the hexafluoride at modest temperatures of the order of 200°. These observations are confirmed by Robb *et al.* (*66*) who found that decomposition products of plutonium hexafluoride can be refluorinated at 200°. The reason for the discrepancy in the effect of temperature on the reaction rate of the fluorination of plutonium tetrafluoride is not clear, but it may be related to differences in the surface area and characteristics of the plutonium tetrafluoride, and on the complex dependence of the reaction on the fluorine pressure. In any event it appears quite certain that

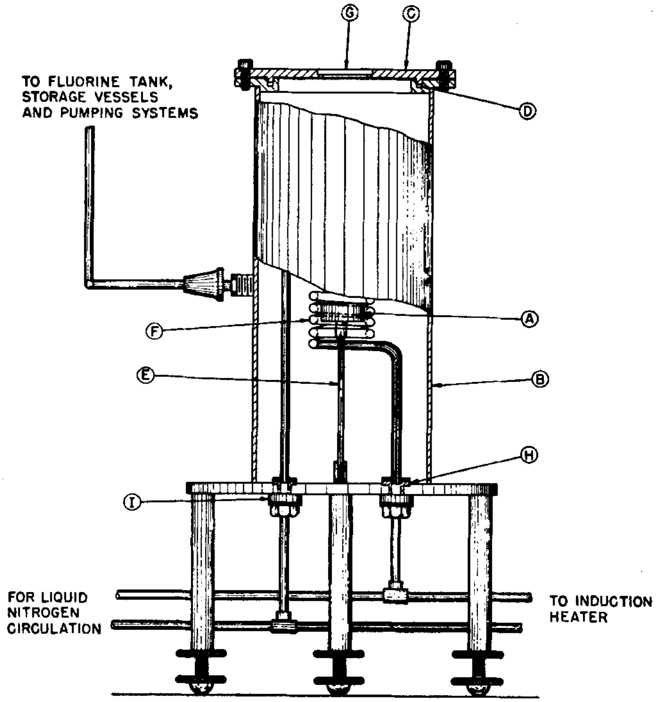

FIG. 7. Reactor for preparation of plutonium hexafluoride (*85*). *A*, nickel dish filled with PuF_4; *B*, brass reactor can; *C*, removable cover for loading reactor; *D*, tongue and groove; Teflon gasket for closure; *E*, nickel supporting rod for nickel dish; *F*, coil of 3/16-in. o.d. copper tubing; *G*, Fluorothene window; *H*, Teflon seal and insulator; *I*, Micalex insulator.

under certain conditions conversion of plutonium tetrafluoride to the hexafluoride can be carried out at a fair rate even at temperatures as low as 170°. These observations have obvious significance for volatility procedures for the recovery of plutonium from neutron-irradiated uranium.

Although the fluorination of PuF_4 is the most useful preparative method, plutonium hexafluoride can be prepared by a variety of alternative reactions (*58*):

$$2PuO_2 + 12HF + O_2 \rightarrow 2PuF_6 + 6H_2O,$$

$$2PuF_4 + O_2 \rightarrow PuF_6 + PuO_2F_2.$$

Although the oxidation of PuF_4 by oxygen very likely proceeds by a mechanism similar to that which obtains in the UF_4-O_2 reaction, details are at the present lacking on the PuF_4-O_2 reaction. The behavior of plutonium trifluoride with oxygen deserves to be noted. When plutonium trifluoride is heated in oxygen at 600°, oxidation to a mixture of plutonium tetrafluoride and plutonium dioxide occurs (*35*, *19*): $4PuF_3 + O_2 \rightleftarrows 3PuF_4 + PuO_2$. The reaction is reversible and oxygen has been observed as a reaction product of plutonium dioxide and plutonium tetrafluoride.

Plutonium hexafluoride is a reddish-brown solid, and like neptunium hexafluoride, is light sensitive. Again, as in the case of uranium and neptunium hexafluorides, plutonium hexafluoride may be handled and stored in quartz or Pyrex equipment with no sign of decomposition provided the glass has been thoroughly outgassed and the hexafluoride is completely free of hydrogen fluoride. Any of the actinide hexafluorides may be heated to 200° in quartz apparatus with little if any attack on the container.

The alpha activity of the actinide elements introduces a complication in assessing the stability of their compounds. Not only does the alpha activity present an extraordinary health hazard in the case of plutonium hexafluoride, and to a lesser extent neptunium hexafluoride, but the continuous passage of alpha particles through the compounds results in radiation decomposition. Shiflett *et al* (*78*) have studied the alpha-particle decomposition of uranium hexafluoride. Compared to plutonium hexafluoride the effects of the self-produced alpha particles are very small. Unless uranium is enriched in U^{234} or U^{235}, radiation effects are very difficult to detect, but uranium enriched a hundredfold in U^{234} or U^{235} emits about 50 times the number of alpha particles as does normal uranium, and here the effects are quite appreciable. In a hundredfold-enriched uranium, about 0.2% of the molecules present would become ionized in the course of a year by self-alpha irradiation and the extent of decomposition might become significant. For normal uranium, the effects of alpha particles on uranium hexafluoride were examined in the gas phase by irradiation with alpha particles from Rn^{222}. The decomposition products of the uranium hexafluoride are fluorine and intermediate uranium fluorides; the products react with each other to reform uranium hexafluoride by a radiation-induced process. The rate of alpha decomposition is essentially independent of the temperature. For G, the number of molecules of uranium hexafluoride decomposed per 100 ev of energy absorbed, a value of 0.90 was found; for M/n, the number of molecules of uranium hexafluoride decomposed per ion pair, a value of 0.27 was calculated. The latter number is based on the assumption of a loss of 30 ev by an alpha particle when it produces one ion pair.

Compounds of plutonium provide a much more striking example of the effects of alpha-particle irradiation than in the case of uranium compounds. This circumstance arises from the very much shorter half-life for alpha decay of Pu^{239} in comparison to that of U^{234} or U^{235}, let alone U^{238}. The rate of radiation decomposition in solid plutonium hexafluoride is about 1.5% per day. From a decomposition rate of 1.5% per day and the assumption that all the energy of the alpha particles is absorbed in the solid, the average energy absorbed in the decomposition of one plutonium hexafluoride molecule is 30 ev. This value is very similar to the average energy loss by alpha particles per ion-pair formation for a wide variety of substances. The decomposition product of plutonium hexafluoride is a green substance that turns white upon exposure to air; both of these products are compounds of plutonium(IV), and no evidence for the formation of plutonium(III) or (V) compounds has been found. The solid radiation decomposition product apparently fails to reach a steady state equilibrium. In order to minimize the loss of plutonium hexafluoride on storage because of radiation damage, it is desirable to store the compound as the vapor. Under these conditions, a considerable fraction of the alpha particles escapes capture and is absorbed in the walls of the container. The pressure of the gas and the geometry of the container thus play important parts in the conservation of the hexafluoride. The lower the pressure of the gas and the smaller the diameter of the containing vessel, the greater will be the probability that a given alpha particle will collide with the wall rather than a plutonium hexafluoride molecule. By appropriate storage conditions the average decomposition rate can be reduced to a value as low as 0.06% per day. It would appear, however, that all of the circumstances relating to the radiation decomposition are not understood, since stabilities considerably greater than would be predicted are on occasion encountered. Clearly, further information regarding the achievement of a steady state, and the conditions under which a back reaction might occur are to be desired.

D. CHLORIDES

The actinide chlorides can be prepared by a variety of more or less standard chemical procedures. As these halides are considerably less volatile than the hexafluorides, the experimental complications and health hazards are considerably reduced. All of the actinide chlorides can be made by direct combination of the elements, but this procedure is seldom resorted to, partly because of the great difficulties encountered in obtaining many of the actinide element metals, and partly because of the difficulty in controlling the reaction. The reaction of halogen with actinide carbides, nitrides, and hydrides very often offers the advantage that the reaction can be more readily controlled. However, such procedures do not obviate the necessity of producing metal, since carbides, nitrides, and hydrides can normally be obtained in a reasonable way only from the metal. If the element is readily available in metallic form, as is the case for thorium, uranium, and plutonium, then the reaction of the actinide hydride with hydrogen chloride is a very convenient procedure:

$$U + \tfrac{3}{2}H_2 \xrightarrow{250°C} UH_3$$

$$UH_3 + 3HCl \xrightarrow{250°\text{–}300°C} UCl_3 + 3H_2.$$

Far more important are procedures involving the chlorination of the oxides. Since the actinide element oxides are very stable in a thermochemical sense, powerful chlorinating agents are required. Thus neither chlorine nor hydrogen chloride will react to any extent with actinide element oxides, and reagents such as carbon tetrachloride, thionyl chloride, phosphorus pentachloride, or phosgene are required. Of these, carbon tetrachloride has perhaps been most widely used. This reagent can be used either in a vapor phase reaction, or in the liquid phase under elevated pressure, and, depending on the exact conditions, UCl_4, UCl_5, or UCl_6 can be obtained from uranium dioxide as the starting material. The chlorination of uranium dioxide and plutonium dioxide by carbon tetrachloride has been the subject of a very thorough investigation by Budaev and Vol'skii (*13*). The complexity of the vapor phase reaction can be judged by the fact that Budaev and Vol'skii find it necessary to postulate some 20 reactions that are supposed to occur during the chlorination of uranium dioxide by carbon tetrachloride. The exhaust gases are found to contain carbon dioxide, phosgene, carbon monoxide, and chlorine. Under conditions of incomplete reaction at 400° to 500°, two intermediate oxychlorides, $UOCl_3$ and $UOCl_2$ are reported to occur; these may be intermediates in the reaction. Uranium(V) oxychloride, $UOCl_3$, consists of reddish-brown crystals that are readily soluble in water, acetone, or methanol, but are insoluble in benzene or carbon tetrachloride. A study was also made of the composition of the solid products and gases formed in the chlorination of plutonium dioxide by carbon tetrachloride at 700°. The principal reactions are:

$$PuO_2 + CCl_4 \rightarrow PuCl_3 + CO_2 + \tfrac{1}{2}Cl_2,$$

$$PuO_2 + 2CCl_4 \rightarrow PuCl_3 + 2CO + \tfrac{5}{2}Cl_2;$$

and to a small extent

$$PuO_2 + 2CCl_4 \rightarrow PuCl_3 + 2COCl_2 + \tfrac{1}{2}Cl_2.$$

Another procedure extensively used for the preparation of plutonium trichloride is the reaction of plutonium oxalate with hydrogen chloride.

Related to carbon tetrachloride is the reagent hexachloropropene, $Cl_3CCCl = CCl_2$; bp, 210°. Uranium trioxide reacts with hexachloropropene at reflux temperature according to the equation (*45*)

$$UO_3 + 3Cl_3CCCl = CCl_2 \rightarrow UCl_4 + 3Cl_2C = CClCOCl + Cl_2.$$

This is perhaps the most convenient method for the preparation of uranium tetrachloride. If the reaction is carried out at lower temperatures, UCl_6 and UCl_5 are the primary products; on heating they lose chlorine to form uranium tetrachloride. Panzer and Suttle (*64*) have reported the isolation of a dark red condensation compound with trichloroacrylyl chloride of the composition $5UCl_5 \cdot CCl_2 = CClCOCl$ that is readily decomposed to uranium tetrachloride. The formation of such a coordination compound by uranium pentachloride is reasonable, as this uranium compound always occurs in a coordinated structure. Pure uranium pentachloride appears to exist as the dimer $(UCl_5)_2$, possibly as (UCl_4^+) (UCl_6^-), and forms coordination compounds with phosphorus pentachloride and thionyl chloride. Hexachloropropene reacts only with uranium oxides in a higher oxidation state, that is, UO_3 or U_3O_8. Uranium dioxide and other dioxides do not react. When Np_3O_8 is treated with hexachloropropene, no reaction is observed (*39*). Plutonium dioxide does not react with hexachloropropene, but plutonium trichloride can be obtained in good yield and purity when plutonium(III) oxalate is heated with hexachloropropene at 180–190° for 18 hr (*16*).

Freeman and Smith (*32*) have prepared the anhydrous chlorides of a number of lanthanides and of thorium by dehydrating the hydrated chlorides with thionyl chloride. Although efforts to obtain anhydrous plutonium trichloride in this way were unsuccessful, it is believed that this may be a useful procedure for actinide elements such as actinium, americium, and curium that have a particularly stable (III) oxidation stage. In general, aqueous methods for preparing tetrachlorides are of little value; but anhydrous trichlorides, particularly of the transuranium elements, can be obtained readily from the hydrated trichlorides by dehydration in an atmosphere of hydrogen chloride.

E. BROMIDES AND IODIDES

Little has appeared since the preparation of such compounds was last reviewed (*51*). Iodides and bromides are best prepared from the elements.

TABLE IV
CRYSTAL STRUCTURE DATA FOR THE ACTINIDE HALIDES[a]

Compound	Color	Crystal structure					
		Symmetry	Space group or structure type	Lattice parameter (Å)[b]			Density (gm/cm³)
				a_0	b_0	c_0	
AcF_3	White	Hexagonal	LaF_3	4.17		7.53	7.88
UF_3	Black	Hexagonal	C_6/mmc	4.146		7.348	8.95
NpF_3	Purple or black	Hexagonal	LaF_3	4.108		7.273	9.12
PuF_3	Purple	Hexagonal	LaF_3	4.087		7.240	9.32
AmF_3	Pink	Hexagonal	LaF_3	4.067		7.225	9.53
CmF_3		Hexagonal	LaF_3				
$AcCl_3$	White	Hexagonal	UCl_3	7.62		4.55	4.81
UCl_3	Red	Hexagonal	$C6_3/m$	7.442		4.320	5.51
$NpCl_3$	White	Hexagonal	$C6_3/m$	7.405		4.273	5.58
$PuCl_3$	Emerald green	Hexagonal	$C6_3/m$	7.380		4.238	5.70
$AmCl_3$	Pink	Hexagonal	$C6_3/m$	7.38		4.25	5.78
$AcBr_3$	White	Hexagonal	UCl_3	8.06		4.68	5.85
UBr_3	Red	Hexagonal	$C6_3/m$	7.942		4.440	6.53
α-$NpBr_3$	Green	Hexagonal	$C6_3/m$	7.917		4.382	6.62
β-$NpBr_3$	Green	Orthorhombic	*Ccmm*	12.65	4.11	9.15	6.62
$PuBr_3$	Green	Orthorhombic	*Ccmm*	12.62	4.09	9.13	6.69
$AmBr_3$	White	Orthorhombic	*Ccmm*	12.6	4.11	9.12	
UI_3	Black	Orthorhombic	*Ccmm*	14.01	4.32	10.01	6.76
NpI_3	Brown	Orthorhombic	*Ccmm*	14.03	4.30	9.95	6.82
PuI_3	Bright green	Orthorhombic	*Ccmm*	14.03	4.30	9.92	6.92
AmI_3	Yellow	Orthorhombic	*Ccmm*	14.0	4.31	9.9	
ThF_4	White	Monoclinic	C^6_{2h}	13.1	11.01 $\alpha_2 = 126 \pm 1°$	8.6	5.71
PaF_4	Reddish brown	Monoclinic	UF_4				

UF_4	Green	Monoclinic	*C*2/*c*	12.82	10.74 $\alpha_2 = 126°10'$	8.41	6.70
NpF_4	Green	Monoclinic	ZrF_4	12.70	10.64 $\alpha_2 = 126°10'$	8.41	6.8
PuF_4	Brown	Monoclinic	*C*2/*c*	12.62	10.57 $\alpha_2 = 126°10'$	8.28	7.0
AmF_4	Tan	Monoclinic	UF_4	12.49	10.47 $\alpha_2 = 126°10'$	8.20	
CmF_4	Greenish tan	Monoclinic	UF_4	12.45	10.45 $\alpha_2 = 126° \pm 30'$	8.16	
$ThCl_4$	White	Tetragonal	*I*4/*amd*	8.473		7.468	4.60
$PaCl_4$	Greenish yellow	Tetragonal	UCl_4	8.377		7.482	
UCl_4	Green	Tetragonal	*I*4/*amd*	8.296		7.487	4.87
$NpCl_4$	Red brown	Tetragonal	*I*4/*amd*	8.29		7.46	4.92
$ThBr_4$	White	Tetragonal		8.963		7.946	5.69
UBr_4[c]	Brown	Monoclinic	2/*c*−/−	10.92	8.69 $\alpha_2 = 93°9'$	7.05	5.55
$NpBr_4$	Reddish brown	Monoclinic	UBr_4				
ThI_4	White						
UI_4	Black						
U_2F_9	Black	Cubic	$I\bar{4}3m$	8.471			7.06
U_4F_{17}	Black		Distorted UF_4				6.94 (exp)
α-UF_5	White	Tetragonal	*I*4/*m*	6.525		4.472	5.81
β-UF_5	White	Tetragonal	$I\bar{4}2d$	11.473		5.209	6.45
UCl_5	Red brown	Monoclinic					3.81 (exp)
UF_6	White	Orthorhombic	*Pnma*	9.900	8.966	5.207	5.060
NpF_6	Brown	Orthorhombic	*Pnma*	9.91	8.97	5.21	5.00
PuF_6	Reddish brown	Orthorhombic					
UCl_6	Black	Hexagonal	$C\bar{3}m$	10.97		6.04	3.56

---

[a] For detailed references to the original literature see Katz and Seaborg (*51*), Seaborg and Katz (*73*), and Katz and Rabinowitch (*50*).

[b] Lattice parameters, when published as kX units, have been converted to Angstrom units.

[c] Douglass and Staritzky (*22*).

Aluminum bromide and iodide, however, have special utility in the conversion of oxides to the corresponding halides. Prigent (*65*) has reported that UO_3 heated with carbon tetrabromide at 165° forms UBr_4. Uranium tetrabromide has also been prepared by reaction of uranium dioxide with a tenfold excess of carbon tetrabromide at 175° and subliming away the UBr_4 formed (*22*).

IV. Properties of Halides

By virtue of the fact that the actinide elements constitute a family of elements whose electronic configurations are related to each other in a quite unique way, a comparison of the physical and chemical properties of a series of related compounds has more than the usual interest. In this section some of the more important properties of the actinide element halides are summarized in tabular form, and a number of topics of current interest are described.

A. STRUCTURE

Crystal structure data obtained by X-ray diffraction methods for the actinide element halides are collected in Table IV. Crystal structure determinations have been most important in identifying new compounds of the actinide elements; the data are sufficiently extensive now for use in drawing conclusions regarding systematic trends and relations among the actinide elements. The tetrafluorides, for instance, supply one of the best illustrations of an actinide contraction that is entirely similar to the well-known lanthanide contraction (Table V).

TABLE V

IONIC RADII OF M^{4+} ACTINIDE IONS[a]

Compound	Ion	Ionic radius (Å)
UF_4	U^{4+}	0.93
NpF_4	Np^{4+}	.92
PuF_4	Pu^{4+}	.90
AmF_4	Am^{4+}	.89
CmF_4	Cm^{4+}	.88

[a] Asprey *et al.* (*6*).

The vibrational spectra of all of the known actinide element hexafluorides can be interpreted on the basis of the structure of a regular octahedron. Malm *et al.* (*56*) have measured the infrared spectra of NpF_6 and PuF_6 and have deduced the fundamental vibration frequencies (Table VI).

Only ν_3 is directly observed in the infrared. All of the frequencies for NpF_6 lie intermediate between UF_6 and PuF_6. The infrared data make it possible to deduce the value of the Raman active frequencies; in the case of uranium hexafluoride, a discrepancy was revealed between the value for the Raman spectrum as deduced by the method of Gaunt (*38*) from infrared measurements and the experimentally determined Raman spectrum of Bigeleisen *et al.* (*10*). Consequently, Claassen *et al.* (*17*) have measured the Raman spectrum of gaseous uranium hexafluoride, and found ν_1 to be 666.6 ± 0.3 cm^{-1} and ν_2, 535 ± 5 cm^{-1}. These new Raman values are in excellent agreement with values deduced by combination from the infrared data, and are the values that appear in Table VI. The infrared and Raman data then lead to the octahedral structure of symmetry O_h for the actinide element hexafluorides.

TABLE VI

FUNDAMENTAL VIBRATION FREQUENCIES OF UF_6, NpF_6, AND PuF_6[a]

Designation	Symmetry species	Spectral activity	Frequencies (cm^{-1})		
			UF_6	NpF_6	PuF_6
ν_1	a_{1g}	Raman, *p*	667	648	628
ν_2	e_g	Raman, *dp*	535	528	523
ν_3	f_{1u}	Infrared	623	624	615
ν_4	f_{1u}	Infrared	181	200	203
ν_5	f_{2g}	Raman, *dp*	202	206	211
ν_6	f_{2u}	Inactive	140	164	171

[a] Malm *et al.* (*56*).

Schomaker *et al.* (*71*) have made an electron-diffraction study of the structure of NpF_6 and PuF_6. An F—F bond angle of exactly 90° is obtained, in agreement with the structure of a regular octahedron, and the derived metal-to-fluorine distances are given in Table VII.

TABLE VII

METAL-FLUORINE BOND LENGTHS OF ACTINIDE ELEMENT HEXAFLUORIDES FROM ELECTRON DIFFRACTION STUDIES[a]

M—F	Distance (Å)
U—F	1.994
Np—F	1.981
Pu—F	1.969

[a] Schomaker *et al.* (*71*).

Here also the metal-fluorine distance decreases with increasing atomic number in a manner analogous to the lanthanide contraction in crystals.

B. VOLATILITY

The actinide element halides run the entire gamut of volatility from very high melting and refractory substances such as the trifluorides to the exceedingly volatile hexafluorides. Table VIII lists the actinide element halides for which quantitative vapor pressure data exist; qualitative observations are collected in Table IX, and data relating to the volatile hexafluorides are given in Table X.

TABLE VIII

VAPOR PRESSURE DATA FOR ACTINIDE ELEMENT HALIDES[a]

Compound	mp (°C)	$\log p_{mm} = -A/T + B$			
		Solid		Liquid	
		A	B	A	B
PuF_3	1425	21120	12.468	19400	11.273
AmF_3		24628	$36.888 - 7.048 \log T$		
UCl_3	835	12000	10.0		
$PuCl_3$	760	15910	12.726	12590	9.509
UBr_3	730	15000	12.5		
$PuBr_3$	681	15281	13.386	12360	10.321
PuI_3		15173	$29.18 - 5.035 \log T$	13008	$30.16 - 6.042 \log T$
ThF_4[b]	1110	16860	11.986	15270	10.821
PuF_4	1037	14370	$36.07 - 7.554 \log T$	18124	$37.97 - 7.554 \log T$
AmF_4[c]		10886	7.727		
$ThCl_4$	770	12910	14.30	7987	9.57
UCl_4	590	10427	13.2995	7205	9.65
$ThBr_4$	679	9628	11.73	7440	9.56
UBr_4	519	10900	14.56	7060	9.71
ThI_4				31500	9.09
U_2F_9[d]	Dec.[e]	7315	13.68		
U_4F_{17}[d]	Dec.	7143	12.75		
α-UF_5[d]	Dec.	2942	7.634		
β-UF_5[d]	Dec.	4166	10.71		

[a] For detailed references to the original literature see Katz and Seaborg (*51*), Seaborg and Katz (*73*), and Katz and Rabinowitch (*50*).

[b] Darnell and Keneshea (*18*).

[c] Yakovlev and Kosyakov (*89*).

[d] Equilibrium vapor pressure of UF_6 for the disproportionation reaction.

[e] Decomposes.

Weinstock *et al.* (*87*) have made an exceedingly thorough study of the vapor pressure of neptunium and plutonium hexafluorides (Table X). The vapor pressures of NpF_6 and PuF_6 are compared to the UF_6 vapor pressures determined by Oliver *et al.* (*63*) in Fig. 8. The relative volatilities of the liquids are in the expected order $UF_6 > NpF_6 > PuF_6$, but the relative volatilities of the solids exhibit a more complicated behavior with NpF_6 having the greatest volatility over the measured solid range. For all molecular parameters such as the vibration frequencies, interatomic distances, and the size of the unit cell in the solids, neptunium hexafluoride is intermediate between the other two actinide hexafluorides. It is, therefore, surprising to encounter such an anomaly in the vapor pressures of the solids. Weinstock *et al.* (*87*) have considered a number of possible explanations to account for the anomalous properties of neptunium hexafluoride. It would appear that explanations based on presumed differences in the Van der Waals forces in the solid or on changes in internal energy do not account for the situation. The suggestion is considered by Weinstock, Weaver, and

TABLE IX

QUALITATIVE OBSERVATIONS ON VOLATILITY OF ACTINIDE ELEMENT HALIDES

Compound	Sublimation temperature (°C)	Compound	Sublimation temperature (°C)
UF_3	<1000	NpI_3	800
$AcCl_3$	950	AmI_3	900
$NpCl_3$	750–800	UF_4	1000
$AmCl_3$	850	$PaCl_4$	400
$AcBr_3$	800	$NpCl_4$	500
$NpBr_3$	800	$NpBr_4$	500
$AmBr_3$	850–900		

TABLE X

VAPOR PRESSURE DATA FOR ACTINIDE ELEMENT HEXAFLUORIDES[a]

Compound	Temperature range (°C)	Vapor pressure equation
$UF_6(c)$[b]	0–64	$\log p_{mm} = 6.38363 + 0.0075377t - 942.76/(t + 183.416)$
$UF_6(l)$[c]	64–116	$= 6.99464 - 1126.288/(t + 221.963)$
$UF_6(l)$	116–230	$= 7.69069 - 1683.165/(t + 302.148)$
$NpF_6(c)$	0–55.10	$= -2892.0/T - 2.6990 \log T + 18.48130$
$NpF_6(l)$	55.10–76.82	$= -1191.1/T + 2.5825 \log T + 0.01023$
$PuF_6(c)$	0–51.59	$= -2095.0/T + 3.4990 \log T + 0.39024$
$PuF_6(l)$	51.95–77.17	$= -1807.5/T - 1.5340 \log T + 12.14545$

[a] Taken from Oliver *et al.* (*63*), and Weinstock *et al.* (*87*).

[b] (c) = crystalline.

[c] (l) = liquid.

Malm that the volatility anomaly of solid NpF_6 is related to the fact that of the three actinide hexafluorides, neptunium hexafluoride is the only one found to be paramagnetic. If the paramagnetism of neptunium hexafluoride is reflected in a higher magnetic entropy for the solid than either its vapor or liquid possesses, an increase in magnetic entropy would also tend to decrease the vapor pressure of the solid. This is in the opposite direction to that actually observed. It may, therefore, be necessary to account for the observations in terms of an electronic effect, in which the ground electronic state of the solid is perturbed relative to the ground state of the vapor to an extent and in the direction which results in a reduced value of the heat of vaporization. A more definitive assessment of the situation must await further experimental data.

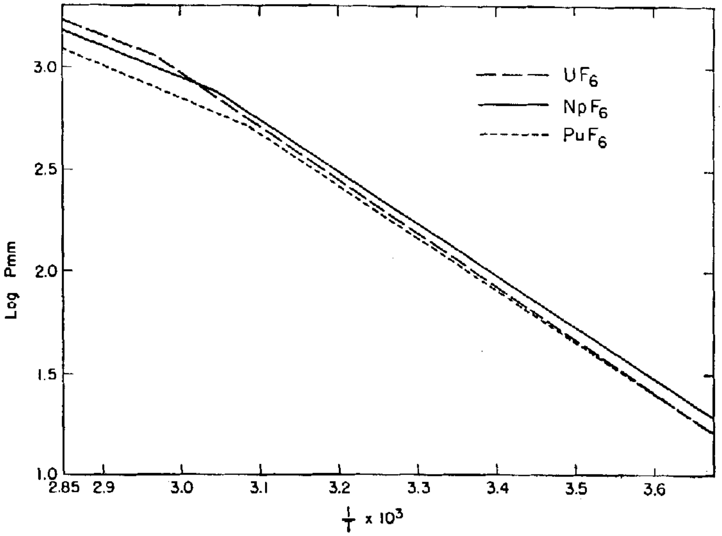

FIG. 8. Vapor pressure of UF_6, NpF_6, and PuF_6 (*67*).

C. CHANGE OF STATE

Thermochemical data for heats of fusion, vaporization, and sublimation are collected in Table XI. Data relating to change in state for the actinide hexafluorides are given in Table XII.

The triple points are seen to decrease in the order UF_6, NpF_6, and PuF_6. It can also be seen that, unlike uranium hexafluoride, neptunium hexafluoride and plutonium hexafluoride possess a liquid range at atmospheric pressure. Heats of sublimation and vaporization are shown in Fig. 9, also taken from the paper of Weinstock *et al.* (*87*).

TABLE XI

THERMOCHEMICAL DATA FOR CHANGE OF STATE OF HALIDES OF ACTINIDE ELEMENTS[a]

Formula	Process	Temperature (°C)	ΔH (kcal/mole)	ΔS (cal/mole/deg)
ThF_4	Sublimation	903	77.1 ± 0.9	41.7
	Vaporization	1511	69.9 ± 1.5	
$ThCl_4$	Sublimation	770	59	55.6
	Vaporization	770	36.5	36.3
	Vaporization	921	35.0	29.3
$ThBr_4$	Sublimation	697	44	47.2
	Vaporization	697	34.5	35.5
	Vaporization	857	30.4	26.9
ThI_4	Vaporization		31.5	
UF_4	Sublimation	1036	68.9	52.6
	Vaporization	1036	63.2	48.3
	Vaporization	1417	57.5	34.1
UCl_3	Sublimation	835	63	57
	Vaporization	835	54	49
UCl_4	Sublimation	590	46.3	53.6
	Vaporization	590	36.0	41.7
UBr_3	Sublimation	752	68.6	66.9
	Fusion	752	11.0	10.7
	Vaporization	752	57.6	56.2
UBr_4	Sublimation	519	41.9	52.9
	Vaporization	519	43.8	43.8
NpF_4	Sublimation	613–818	71.8	46.2
PuF_3	Sublimation	1056	96.6	72.9
	Fusion		7.9	5.5
	Vaporization	1289	88.7	51.8
PuF_4	Sublimation	500–851	68.0	46.2
$PuCl_3$	Sublimation	760	72.8	63
	Fusion		15.2	14.7
	Vaporization	760	57.6	57.8
$PuBr_3$	Sublimation	681	69.9	74.0
	Fusion		13.4	14.0
	Vaporization	681	56.5	60.0
PuI_3	Fusion		(12)	
AmF_3	Sublimation		112.67 ± 0.12	
AmF_4	Sublimation	385–640	49.8	22.2

[a] For detailed references to the original literature see Katz and Seaborg (*51*), Rossini *et al.* (*67*), Darnell and Keneshea (*18*), and Yakovlev and Kosyakov (*89*).

D. THERMOCHEMISTRY

Heats and entropies of formation are assembled in Table XIII. It is somewhat disconcerting to realize that many of the values given in the table are estimates, and that experimental values are still lacking.

TABLE XII

DATA RELATING TO PHASE TRANSITIONS FOR HEXAFLUORIDES OF THE ACTINIDE ELEMENTS[a]

Compound	Boiling or sublimation point (°C)	Vapor pressure at 0°C (mm of Hg)	Triple point (°C)	Triple point mm of Hg	Heat of fusion (cal/mole)	Entropy of fusion (cal/mole/deg)
UF_6	56.54	17.65	64.05	1139.6	4588	13.61
NpF_6	55.18	20.8	55.10	758.0	4198	12.79
PuF_6	62.16	17.9	51.59	533.0	4456	13.72

[a] Weinstock *et al.* (*87*).

One interesting point that requires mention is the question of the thermodynamic stability of plutonium hexafluoride. Weinstock and Malm (*85*) have concluded that plutonium hexafluoride is unstable toward dissociation by the reaction

$$PuF_6 \leftrightarrows PuF_4 + F_2.$$

Thermal decomposition appears to be quite small at 200°, but decomposition of the hexafluoride is practically complete at 280° in 1 hr. The thermodynamic instability of plutonium hexafluoride toward dissociation has the consequence that the hexafluoride becomes more stable as the temperature is raised. In spite of the evidence that indicates that plutonium hexafluoride is a thermodynamically unstable substance, it can be stored for long periods of time at room temperature with rather small losses. This suggests the possibility that in the course of thermal decomposition the reaction does not come to equilibrium; it is known that the reverse reaction,

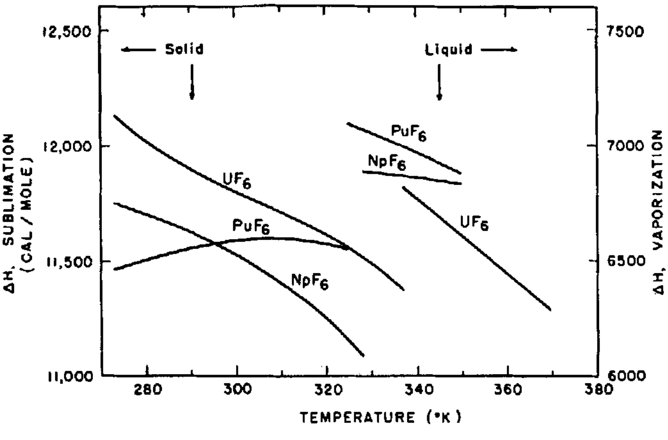

FIG. 9. Heats of sublimation and vaporization of UF_6, NpF_6, and PuF_6 (*87*).

TABLE XIII

Heats and Entropies of Formation of Actinide Element Halide[a,b]

Formula[c]	ΔH_f° (kcal/mole)	ΔF_f° (kcal/mole)	S° (cal/mole/deg)
AcF_3	(−410 ± 10)		
$AcCl_3$	(−260 ± 10)		
$AcBr_3$	(−220 ± 10)		
AcI_3	(−169 ± 10)		
ThF_4	(−478)		33.95 ± 0.4
$ThCl_4$	−284.5 ± 0.5		(48.3)
$ThBr_4$	−229		
ThI_4	−132		
PaF_4	(−477)		
UF_3	(−357)	(−339)	(26)
UF_4	−443 ± 3	−421	36.93 ± .2
U_4F_{17}	−1820.5	−1727.5	149.0
U_2F_9	−933.8	−884.0	75.3
α-UF_5	−483.7	−458.2	48.0
β-UF_5	−485.2 ± 1.5	−458.7 ± 1.5	43.3 ± .5
UF_6(g)	−505	−485	90.76 ± 1
UF_6	−517	−486	54.45
UCl_3	−213.0 ± 1.5	−196.9	37.99
UCl_4	−251.2 ± 0.5	−230.0	47.4
UCl_5	−262.1 ± 0.5	(−237.4)	(62)
UCl_6	−272.4 ± 0.6	−241.5	68.3
UBr_3	−170.1 ± 0.7	(−164.7)	(49)
UBr_4	−196.6 ± 0.5	(−188.5)	(58)
UI_3	−114.7 ± 0.7	(−115.3)	(56)
UI_4	−127.0 ± 0.7	(−126.1)	(65)
NpF_3	(−360 ± 2)		
NpF_4	(−428 ± 3)		
NpF_6(g)	(−463 ± 3)		
$NpCl_3$	(−216 ± 2)		
$NpCl_4$	(−237 ± 1)		
$NpCl_5$	−246[d]		
$NpBr_3$	(−174 ± 1)		
$NpBr_4$	(−183 ± 1)		
NpI_3	(−120 ± 1)		
PuF_3	−374.6 ± 0.5	(−356)	
PuF_4	(−424 ± 4)	(−400)	(37.9 ± 0.5)
PuF_6(g)	(−392)		88.31
$PuCl_3$	−230.1 ± 0.3	(−214)	(38)
$PuBr_3$	−187.8	(−182.4)	(49)
PuI_3	(−133 ± 1)	(−133.6)	(56)
AmF_3	(−394)		
AmF_4	(−400)		
$AmCl_3$	−251.3		

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[a] Values in this table are from Katz and Seaborg *(51)*.

[b] Parentheses are estimated values.

[c] For the solid state unless otherwise indicated.

[d] Rossini *et al.* *(67)*.

the refluorination of plutonium tetrafluoride, is a slow reaction at low temperatures. An experimental determination of the heat of formation of plutonium hexafluoride will be required before the point can be settled. This is a matter of considerable difficulty because the reaction of plutonium hexafluoride with water is a complex one. It produces plutonium in all of its oxidation states in variable amounts, along with variable amounts of oxygen, ozone, and perhaps oxygen fluoride. Consequently a simple measurement of the heat of solution does not seem to provide the means whereby the heat of formation can be deduced.

E. Electronic Configuration

Both uranium hexafluoride and plutonium hexafluoride (*42*) possess a small temperature-dependent paramagnetism. The slight paramagnetism of uranium hexafluoride is expected because all of its valence electrons are paired in the six fluoride bonds of UF_6. For PuF_6, the situation is surprising. Plutonium hexafluoride contains two nonbonding $5f$ electrons and might, therefore, be expected to be strongly paramagnetic. The absence of paramagnetism in plutonium hexafluoride has been explained as a result of the octahedral electric field produced by the six fluoride ions. In such a field, an f-term is split into three levels, f_β, f_δ, and f_ϵ, with f_β, corresponding to the one-dimensional representation Γ_2, lying lowest. If the two nonbonding electrons in plutonium hexafluoride are regarded as occupying the f_β level with paired spins, then the small susceptibility observed for plutonium hexafluoride can be accounted for. The magnetic susceptibility of neptunium hexafluoride has been measured by Weinstock and Malm (*86*). Neptunium hexafluoride, like other actinide compounds containing nonbonding electrons, shows a fairly large temperature-dependent magnetic susceptibility. The octahedral field provided by the fluoride ions results in an unusual behavior for the paramagnetism of NpF_6. The susceptibility values are markedly smaller at corresponding temperatures than those observed for the isoelectronic compound sodium neptunyl acetate, $NaNpO_2(CH_3COO)_3$, or than those calculated for the spin-only and unquenched orbital angular momentum cases.

The oxidation number +4 is not known in aqueous solutions of americium and curium. The measurement of the absorption spectra of americium and curium tetrafluorides by Asprey and Keenan (*7*) is thus a valuable contribution to the study of the electronic spectra of the actinide elements. Special techniques were devised to measure these spectra with microgram amounts of CmF_4 and AmF_4 over the region 3500–20000 Å. Table XIV lists the positions and the relative intensities of the observed maxima. The agreement of the trivalent fluoride spectra with those of the corresponding

TABLE XIV

ABSORPTION SPECTRA MAXIMA (Å) OF TRI- AND TETRAFLUORIDES OF CURIUM AND AMERICIUM[a] (ASPREY AND KEENAN, 7)

AmF_3	CmF_3	AmF_4	CmF_4
3600 w	3740 m	3760 s	3865 m
3652 w	3780 m	4530 s	4010 m
3760 m	3950 s	4860 w	4118 m
4003 w	4490 w	5360 w	4504 s
4150 w		5680 s	4607 m
4378 w		6390 m	6730 w
4530 w		7030 m	6960 w
5006 s		7440 m	7650 w
5085 s		8620 m	7915 w
5148 m		9180 m	8560 s
7900 s			9100 w
8250 w			10975 w
9015 w			16120 w
9918 w			
10460 m			
10660 w			
11120 w			

[a] s, sharp peak; m, moderately sharp peak; w, weak or very broad peak.

trivalent ions is very close. Absorption in $4f^7$ gadolinium(III) is confined to regions below 3200 Å. The electronic transitions of $5f^7$ curium(III) lie at lower energies because the absorption bands are moved towards the visible. This shift, as well as the very existence of curium(IV), emphasizes that the $5f$ electrons in the actinide elements are less tightly bound than the corresponding $4f$ electrons in the lanthanide elements.

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