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PLUTONIUM HANDBOOK - SECTION III - THE CHEMISTRY OF PLUTONIUM

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SECTION III THE CHEMISTRY OF PLUTONIUM

CHAPTER 1

CHEMICAL PRINCIPLES

Jesse M. Cleveland, Jr.

Hanford Atomic Products Operation

SECTION III

THE CHEMISTRY OF PLUTONIUM

Many significant advances have been made in the chemistry of plutonium since the publication of the most recent review[1] of the subject in 1957. Primarily as a result of the Geneva Conferences, much of the classified literature on plutonium chemistry has been declassified and made available to the general scientific community. In addition, most of the current research, concerned primarily with the kinetics of plutonium reactions and the preparation and determination of the properties of complexes and new solid compounds of plutonium, is published in the open literature soon after completion. The result has been an impressive addition to the fund of knowledge on plutonium chemistry within the past few years.

The aim of the present review is to make this knowledge, both new and old, available in a convenient and unified form to workers in the field of plutonium chemistry. The emphasis is placed on experimental data and the conclusions drawn therefrom, although theory will be discussed in sufficient detail to place the data in proper perspective. It is anticipated that the final result will be a reliable, thorough, and up-to-date survey of plutonium chemistry through 1961.

SECTION III THE CHEMISTRY OF PLUTONIUM

CHAPTER 1

CHEMICAL PRINCIPLES

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CHEMICAL PRINCIPLES

By Jesse M. Cleveland, Jr.

1-1 THE ACTINIDE THEORY

Although the existence of a second rare-earth-like series, in the seventh row of the periodic table, had been suggested as early as 1925,[2] it was not until the discovery of the transuranium elements that this theory gained wide acceptance. In 1945, Seaborg[3] postulated that actinium and the transactinides formed such a series, in which the 5f electron shell was being completed in a manner analogous to the filling of the 4f shell in the lanthanide series. This theory was initially attractive because of the pronounced lack of chemical similarity between neptunium and rhenium and between plutonium and osmium; it has since been supported by a preponderance of evidence.

Magnetic susceptibility measurements have provided support for the actinide theory. Values for actinide ions in solution, though somewhat lower than theoretical, varied in the same manner as those for the corresponding lanthanide ions.[4] Molar magnetic susceptibilities of plutonium (III) and plutonium (IV) ions in solution at 20°, 370 x 10^{-6} and 1610 x 10^{-6}, respectively, can be interpreted only on the basis of $5f^5$ and $5f^4$ electron configurations for these ions.[4] Susceptibilities of plutonium trifluoride and trichloride were determined at temperatures from 90 to 600°, and provided further evidence for a $5f^5$ configuration for plutonium (III).[5]

Magnetic susceptibilities of plutonium tetrafluoride and plutonium dioxide have been measured from 90 to 450°K by Dawson.[6] The tetrafluoride was found to obey the Curie-Weiss law above 200°K, while the dioxide failed to obey the law at any temperature. Data for the tetrafluoride in solid solution in thorium tetrafluoride agree with a $5f^4$ configuration for plutonium (IV); susceptibility data for the dioxide tend to support this configuration, but also offer some evidence that the 6d levels are occupied. Lewis and Elliott[7] measured the magnetic susceptibilities of $Pu(SO_4)_2 \cdot 4H_2O$, $Rb_4Pu(SO_4)_4 \cdot 2H_2O$, $Pu(C_2O_4)_2 \cdot 6H_2O$, $[(CH_3)_4N]_2 PuCl_6$, and PuF_4 from 77 to 334°K; the failure of these compounds to obey the Curie-Weiss law was discussed in terms of the crystalline field symmetry.

The magnetic susceptibility of sodium plutonyl acetate was determined in the temperature range 90 - 300°K, and found to follow the Curie-Weiss law exactly.[8] The fact that the susceptibility agrees with the theoretical spin-only value for two unpaired electrons is taken as evidence that the plutonyl ion has a $6d^2$ electron configuration. This configuration is most unlikely, and has been contradicted by other data. Thus the paramagnetic resonance absorption of the same compound at 4°K, measured by Hutchinson and Lewis,[9] indicates the presence of two 5f electrons in the plutonyl ion.

The ion exchange behavior of the trivalent actinides is closely comparable to that of the lanthanides. Since f-orbitals are shielded from their environment more than the outer orbitals, the absorption spectra of the trivalent lanthanides contain sharper bands than those of other elements. The spectra of the trivalent actinides display similarly sharp absorption bands. The analogy between spectra of lanthanide and actinide elements is very close for the trivalent ions; for ions in other oxidation states, however, only the actinides exhibit sharp absorption bands.[10]

Although the existence of this second rare-earth series has been generally accepted, there are several important differences between the lanthanide and actinide elements. While the trivalent state is most stable for all of the lanthanides, such is not the case for the early members of the actinide series. Thus, for thorium, protoactinium, uranium, neptunium, and plutonium the most stable oxidation states are 4, 5, 6, 5, and 4 respectively. From americium through the remainder of the series, the trivalent state is dominant, and the resemblance to the lanthanides is more striking. The anomaly in the early members of the series is due principally to the very small difference in energy levels between 5f and 6d orbitals; since this energy difference is of the same order of magnitude as chemical binding energies, the electron configurations (and consequently the oxidation states) of these elements are more sensitive to chemical environment than is the case for the lanthanides, where there is a greater energy difference between 4f and 5d orbitals.

The uncertainty in electron configurations for the elements thorium-plutonium has led to some disagreement as to the parent element of the series. Thus, Haissinsky[11] feels that the differences in properties between thorium, protoactinium, and uranium, as well as the similarities of these elements to hafnium, tantalum, and tungsten, justifies transferring them back to groups IVa, Va, and VIa, respectively. Dawson[12] goes a step further by suggesting that a "uranide" series, consisting of uranium, neptunium, plutonium, and americium, be placed in group VIa, and that the remaining transuranium elements (the "curides") be placed under actinium in group IIIa. Villar[13] accepts, in general, the actinide hypothesis, but with a few modifications. He places the actinides, as well as the lanthanides, between groups IIa and IIIa, with lutecium and element 103 (the recently-discovered "lawrencium") occupying group IIIa.

While the actinide theory has met with almost universal acceptance, it is worth noting, as Makarov[14] points out, that in their higher oxidation states, the early members of the actinide series (including plutonium) have similarities to the elements of groups IVa, Va, and VIa, particularly in their crystal chemistry. The desirability of having each element occupy only one position in the periodic table, however, dictates that even the early members of the actinide series be placed in positions corresponding tc their lanthanide analogs.

1-2 ATOMIC AND IONIC SIZES

Just as there is a gradual contraction in atomic and ionic radii from lanthanum to lutetium (the "lanthanide contraction"), so there is an "actinide contraction". Such would be expected, and furnishes further confirmation of the presence of 5f electrons in the actinide elements. These size variations are important in determining relative complex-forming tendencies and ion-exchange adsorptions, and are therefore of significance in chemical separations processes. Table 1.1 gives radii for plutonium and its nearest neighbors in compounds having predominantly metallic, ionic, and covalent bonding.

Table 1.1 - METALLIC, IONIC, AND COVALENT RADII[15]

Element	Metallic Radii*, A Valence State				Ionic Radii, A Valence State				Single-Bond Covalent Radii, A Valence State		
	+3	+4	+5	+6	+3	+4	+5	+6	+4	+5	+6
Uranium	1.92	1.74	1.61	1.54	1.03	0.93	0.87	0.83	1.62	1.50	1.42
Neptunium	1.89	1.72	1.60	1.52	1.01	0.92	0.88	0.82	1.60	1.49	1.41
Plutonium	1.86	1.70	1.59	1.51	1.00	0.90	0.87	0.81	1.58	1.48	1.40
Americium	1.84	1.69	1.58	1.50	0.99	0.89	0.86	0.80	1.57	1.47	1.39

*Only the values for uranyl (VI) and neptunyl (VI) were determined experimentally; the remainder are interpolated or extrapolated values. Data are for a coordination number of 12.

1-3 CHEMICAL PROPERTIES OF PLUTONIUM METAL

In the absence of surface oxidation, plutonium is a silvery-white metal resembling iron or nickel. It is oxidized by air at a rate dependent on relative humidity: at approximately zero per cent relative humidity the rate is lower by a factor of 100 to 1000 than that at 50 per cent relative humidity.[16] As surface oxidation proceeds, the metal acquires a bronze-like interference color; further oxidation causes a gun-metal blue color, and finally the metal turns dull black or green due to the formation of a loose coating of oxide. The atmospheric oxidation of plutonium is discussed in greater detail in Sec. II, Chap. 4.

Because of its highly electropositive nature, plutonium metal is soluble in a number of mineral acids. The affect of various solutions on the metal is shown in Table 1.2.

Operating details for the dissolution of plutonium in various acids are given in Sec. IV, Chap. 3. The corrosion of plutonium metal is discussed in Sec. II, Chap. 4.

Table 1.2 - REACTIVITY OF PLUTONIUM IN VARIOUS SOLUTIONS[16]

Solutions	Reactivity
Water	Reacts very slowly at room temp., slightly faster at the boiling point.
Nitric Acid	No attack at any concentration because of passivation; in the presence of 0.005 M HF, the boiling concentrated acid will dissolve plutonium fairly rapidly.
Hydrochloric and Hydrobromic Acids	Very rapid dissolution by concentrated and moderately dilute acids.
Hydrofluoric Acid	Very slowly attacked. Briquets made by pressing Pu metal turnings will often dissolve rapidly and completely, forming insoluble PuF_3.[17]
Perchloric Acid (72%)	Rapid Dissolution.
Sulfuric Acid	Concentrated acid forms protective coating on the metal which causes initially slow reaction to stop. Moderately dilute acid (5 N) attacks the metal slowly; occasionally impure samples of the metal may be dissolved completely in 5 N acid.
Phosphoric Acid (85%)	Attacked fairly rapidly.
Acetic Acid	Unattacked by glacial acid, even when hot; slow attack by dilute acid.
Trichloroacetic Acid	Rapid dissolution by concentrated acid; slower attack by dilute acid.

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SECTION III THE CHEMISTRY OF PLUTONIUM

CHAPTER 2

COMPOUNDS OF PLUTONIUM

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CHAPTER 2

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The compounds of plutonium have been intensively studied, and are now quite well known. Plutonium (III) and (IV) form a number of stable compounds; to date, however, only a few compounds of plutonium (V) and (VI) are known, and they are less stable than the corresponding uranium compounds. Plutonium compounds tend to vary slightly in stoichiometry and hydration depending on the method of preparation; careful control of conditions is required, therefore, to prepare compounds suitable as primary standards for plutonium.

2-1 PLUTONIUM HYDRIDES

Plutonium hydrides of composition PuH_2 and PuH_3 have been prepared by direct combination of the elements. Under the usual preparative conditions, however, a nonstoichiometric material of intermediate composition results; thus, if hydrogen is allowed to react freely with plutonium at 150 - 200°, a product having the approximate composition $PuH_{2.7}$ is obtained.[1] The reaction apparently proceeds by the initial formation of PuH_2, which then dissolves hydrogen in the interstices, with a decrease in lattice parameter.[2,3] At a H/Pu ratio of about 2.75, hexagonal PuH_3 begins to form; this exists in solid solution with the cubic phase until a H/Pu ratio of about 2.9 - 3.0 is reached, at which point only the hexagonal phase remains. X-ray crystal structure data for the hydrides are given in Table 2.1.

Mulford and Sturdy[2] studied the equilibrium between plutonium-hydrogen and plutonium-deuterium systems from 400 to 800° and from these results estimated the lower composition limits of plutonium dihydride at various temperatures as shown in Table 2.2. They interpreted the nonstoichiometry to be due to one of three possible causes:

(1) vacant hydrogen positions,

(2) presence of plutonium atoms in some of the hydrogen positions, or

(3) presence of interstitial plutonium.

The data do not allow a choice between those three possibilities.

The rate of attainment of equilibrium in the plutonium-hydrogen system varies from less than an hour at 700° to 20 hours at 450°.

A plot of decomposition pressures versus temperature enabled Mulford and Sturdy to calculate the heats of formation of PuH_2 and PuD_2:

$$Pu + H_2(g) \rightleftarrows PuH_2(s) \qquad \Delta H = -37.4 \pm 1.2 \text{ kcal/mole}$$

$$Pu + D_2(g) \rightleftarrows PuD_2(s) \qquad \Delta H = -35.5 \pm 0.7 \text{ kcal/mole}.$$

Table 2.1 - CRYSTAL STRUCTURE DATA FOR PLUTONIUM HYDRIDES[5]

Composition	Symmetry	Space Group	Lattice Parameters, A		Formula Units per Unit Cell	Calculated Density, g/cm^3
			a_o	c_o		
$PuH_{2.0}$ - $PuH_{2.7}$	Face-centered Cubic	$Fm\bar{3}m$	$PuH_{2.0}$: 5.359 ± 0.001 $PuH_{2.5}$: 5.34 ± 0.01		4	10.40
PuH_3	Hexagonal	$P6_3/mmc$	3.78	6.76	2	9.61

Table 2.2 - LOWER COMPOSITION LIMITS FOR PLUTONIUM DIHYDRIDE[2]

Temp., °C	H/Pu Ratio
500	1.88
600	1.86
650	1.86
700	1.85
750	1.80
800	1.75

The following empirical equations were obtained for the decomposition pressures of the dihydride and dideuteride:

$$PuH_2: \quad \log_{10} P(\text{mm Hg}) = 10.01 \pm 0.32 - (8165 \pm 263)/T(^\circ K)$$

$$PuD_2: \quad \log_{10} P(\text{mm Hg}) = 9.71 \pm 0.19 - (7761 \pm 151)/T(^\circ K)$$

These equations were used to calculate the values listed in Table 2.3. Under one atmosphere pressure of hydrogen, plutonium dihydride is stable at temperatures as high as 1000°C.[4]

Plutonium trihydride, a black solid, is much less stable than the dihydride; at 25° it has a decomposition pressure of 350 mm of mercury.[5]

Plutonium hydride of composition $PuH_{2.7}$ is a hard, black, metallic-appearing material.[1] It is inert toward cold water, but reacts slowly at 90°, with gas evolution. The behavior of the hydride towards acids resembles that of the metal. Thus it does not react with nitric acid, but dissolves readily with effervescence in 0.1 - 10 molar hydrochloric acid and more slowly in 3 molar sulfuric acid, in both cases producing a plutonium (III) solution. The hydride is stable in air up to 150°.

Plutonium hydrides are formed during atmospheric corrosion of plutonium metal; larger quantities result when corrosion takes place in the absence of oxygen.[6]

Table 2.3 - DECOMPOSITION PRESSURES OF PuH_2 AND PuD_2[2]

Temperature, °C	Decomposition Pressure mm Hg	
	PuH_2	PuD_2
400	0.008	--
450	0.052	--
500	0.278	--
550	1.23	--
600	4.58	6.61
650	14.7	20.0
700	41.3	53.6
750	105.9	131.0
800	251.2	297.0

2-2 PLUTONIUM OXIDES

Because of their promising potential use as reactor fuels, plutonium oxides are receiving considerable study, and their ceramic properties are described in detail in Sec. II, Chap. 6. The present discussion will be limited to topics primarily of chemical interest, namely the formation and chemical properties of the oxides.

Plutonium has a strong (sometimes pyrophoric) affinity for oxygen, forming two sesquioxides and the dioxide, the latter being the most stable and the one formed under most conditions. In addition, X-ray Debye patterns of surface oxide films have been ascribed to plutonium monoxide, but efforts to prepare it appear to have been unsuccessful.[7] Its existence must therefore be regarded with doubt until there is more conclusive evidence.

2-2.1 Plutonium Dioxide. Plutonium dioxide is formed when plutonium or its compounds (except the phosphates) are ignited in air, and often results when oxygen-containing compounds are heated in vacuo or in an inert atmosphere to 1000°. Holley and coworkers[7] have made the dioxide by the ignition of plutonium (III) or (IV) oxalate, or plutonium (IV) peroxide. It is important that the starting compound be precipitated in a crystalline form. Gelatinous precipitates tend to produce black, impure oxides on ignition.

Plutonium dioxide may be prepared in a pure, crystalline form by heating plutonium (III) or (IV) oxalate to 1000° in air. To avoid rapid decomposition the heating rate must be slow up to about 700°, after which the temperature is raised (more rapidly) to 1000° to remove the last traces of carbon. The peroxide is ignited in a similar manner, except that it must be heated especially slowly to about 200° to prevent spattering due to rapid decomposition. Heating to 700° will remove sulfate. Once again, heating to 1000° is recommended to insure a product of high purity.

Drummond and Welch[8] studied the stoichiometry of the dioxide as a function of its preparative history. They found that the O/Pu ratio of dioxide produced by ignition at 870° depended on the source material, as shown in Table 2.4. Upon ignition to 1200°, however, the oxides approached stoichiometry, with O/Pu ratios of 2.002 ± 0.008. Using more precise equipment, Waterbury et al.[9] have found that plutonium (IV) sulfate and oxalate must be ignited to temperatures above 1250° in order to form stoichiometric plutonium dioxide; at lower temperatures a slight excess of oxygen is present. (For an unknown reason, ignition of plutonium (IV) nitrate at 1250° produces plutonium dioxide that is oxygen-deficient; it would therefore appear that stoichiometric dioxide cannot conveniently be produced by ignition of the nitrate.) Thus the preparative methods described above should be revised to include ignition to temperatures above 1250° if the stoichiometric dioxide is required.

Plutonium dioxide is normally green, but the color, being a function of purity and particle size, varies with the method of preparation. Thus Drummond and Welch[8] prepared plutonium dioxide by igniting a number of different plutonium compounds at 870°; the color of the dioxide resulting from various source compounds is shown in Table 2.5. All of these samples turned to a darker, khaki color upon ignition at 1200°.

Plutonium has a great affinity for oxygen, as evidenced by the fact that oxide has been observed to form on the metal even in evacuated systems at pressures of less than one micron.[10] The heat of formation of plutonium dioxide has been accurately determined by burning the metal in a bomb calorimeter. Popov and Ivanov[11] obtained a value of $\Delta H^\circ_{298} = -252{,}400 \pm 1{,}100$ cal/mole, while Holley and coworkers[7] found $\Delta H^\circ_{298} = -252{,}870 \pm 380$ cal/mole. Using their value for ΔH°_{298} and Coughlin's[12] estimates for ΔS°_{298} (-42.0 cal/degree/mole) and ΔCp (1.5 cal/degree), both of which seem

Table 2.4 - O/Pu RATIO OF PLUTONIUM DIOXIDE IGNITED AT 870°[8]

Source	O/Pu Ratio
Plutonium Metal	2.015
Sulfate	2.089
Nitrate	2.046

Table 2.5 - QUALITATIVE CHARACTERISTICS OF PLUTONIUM DIOXIDE FROM VARIOUS SOURCES IGNITED AT 870°C

Source	Color	Appearance
Sulfate	Yellow-green to green	Bulky powder
Nitrate	Dull yellow	Bulky solid
Chloride	Dull yellow	Powder
Fluoride	Khaki with black traces	Granules
Oxalate	Yellow-buff	Bulky powder
Iodate	Buff	Very bulky
Hydroxide	Black with yellow traces	Dense shiny particles

reasonable, Holley et al. calculated the heat and free energy of formation of plutonium dioxide at various temperatures. Table 2.6 lists their results. The free energy equation for the temperature range 25 - 1200° is:[7]

$$\Delta F^{\circ} \text{ (cal/mole)} = -253{,}480 - 3.45T \log T + 52.48T$$

X-ray crystallographic data for the plutonium oxides are given in Table 2.7.[5]

Plutonium dioxide, particularly that prepared at high temperatures, is a very refractory material, difficult to dissolve by normal techniques. Holley et al.[7] recommend the following solvents, listed in order of decreasing effectiveness: 85 - 100 per cent phosphoric acid at 200°, 10 molar nitric acid- -0.05 molar hydrofluoric acid, and 5 molar hydriodic acid. The ability of boiling nitric-hydrofluoric acids to dissolve plutonium dioxide is often cited; in point of fact, the high-temperature oxide dissolves only very slowly in this acid mixture. The rate of dissolution is much greater in boiling hydrobromic acid, whose effectiveness is apparently due to the fact that it is both a strong acid and a reducing agent.[13]

Often it is possible to dissolve plutonium dioxide by fusion techniques. Methods have been reported based on fusion in sodium bisulfate,[8] potassium pyrosulfate,[14] and ammonium bifluoride.[15]

Plutonium dioxide may be fluorinated to the trifluoride or the tetrafluoride, but once again the reaction proceeds extremely slowly with the high-temperature oxide.

The decreased reactivity of PuO_2 prepared by ignition at higher temperatures appears to be due to perfection of the crystal lattice. Bjorklund and Staritzky[16] found that the refractive index of the dioxide prepared from Pu(IV) oxalate increased from 1.9 to 2.4 as the ignition temperature was increased from 150 to 1000°. (Oxide prepared by ignition of the metal at 170° had a refractive index of 2.40, and was unchanged at higher temperatures.)

Table 2.6 - HEAT AND FREE ENERGY OF FORMATION OF PLUTONIUM DIOXIDE[7]

T, °K	$-\Delta H^\circ$ (cal/mole)	$-\Delta F^\circ$ (cal/mole)
298.16	252,900(±500)	240,400(±800)
383(α)*	252,800	236,800
383(β)*	253,700	236,800
400	253,700	236,100
500	253,500	231,900
593(γ)*	253,400	228,000
593(ζ)*	254,100	228,000
600	254,100	227,700
700	253,900	223,600
800	253,800	219,500
900	253,600	215,400
913(ε)*	253,600	214,900
913(liq.)	254,100	214,900
1000	254,000	211,400
1100	253,800	207,300
1200	253,700	203,300
1300	253,500	199,200
1400	253,400	195,200
1500	253,200	191,200

*Greek letters in parenthesis refer to allotropic modifications of plutonium and are given at transition temperatures.

Table 2.7 - X-RAY CRYSTALLOGRAPHIC DATA FOR PLUTONIUM OXIDES[5]

Composition	Symmetry	Space Group	Lattice Parameters A a_o	Lattice Parameters A c_o	Formula Units per Unit Cell	Calculated Density (g/cm^3)
PuO(?)	Face-centered cubic	Fm3m	4.96±0.01		4	13.9
Pu_2O_3	Hexagonal	$P\bar{3}ml$	3.841±0.006	5.958±0.005	1	11.47
Pu_2O_3-Pu_4O_7	Body-centered cubic	Ia3	11.04±0.02		16	10.2
PuO_2	Face-centered cubic	Fm3m	5.3960±0.0003		4	11.46

The X-ray diffraction pattern changed from weak, diffuse lines for the 150° oxide to sharp lines for the 1000° material. Also, the rate of dissolution in hydrochloric acid-potassium iodide decreased markedly as the ignition temperature was raised. All of these factors indicate that perfection of the originally highly-distorted (and nonstoichiometric) plutonium dioxide lattice is responsible for the refractive nature of the high-temperature oxide. These results, considered in the light of the discussion above regarding the nonstoichiometry of low-temperature oxides, suggest the possibility that the lattice distortions, and hence the reactivity, of these materials may be due at least in part to the presence of interstitial oxygen.

By means of a modified Knudsen effusion method, Phipps, Sears, and Simpson[17] have obtained vapor pressure data for plutonium dioxide. From 1320 to 1520°, thermal reduction of PuO_2 appears to take place, with the formation of oxides in the Pu_4O_7 region. As reduction proceeds, the partial pressure of the oxide present in the vapor phase gradually increases. When the partial pressure of this volatile oxide reaches a value some four or five times that characteristic of plutonium dioxide, a steady state is reached, above which reproducible vapor pressures may be obtained. Thus in the 1520 - 1790° temperature range, the vapor pressure was found to follow the equation

$$\log P \text{ (mm Hg)} = 11.010 - 27{,}910/T \text{ (°K)}.$$

The steady-state oxide may be reoxidized to the dioxide by heating in a low-pressure oxygen atmosphere.

2-2.2 Plutonium Sesquioxide. There are two forms of Pu_2O_3, one hexagonal and one cubic, both of which can be prepared from the dioxide.[7] The more common hexagonal form is made by reducing plutonium dioxide with an excess of finely-divided plutonium metal or hydride in a closed tantalum crucible for three hours at 1500°. If the hydride is used, heating must be

slow until the hydrogen is driven off. The black, sintered Pu_2O_3 thus produced contains metallic plutonium, which may be removed by evaporation in an open crucible at 1800 - 1900° in vacuo. The oxide tends to be pyrophoric if ground, but is stable toward air oxidation for several days if not disturbed. A crystalline Pu_2O_3 may be produced by performing the reduction at a higher temperature. The heat of formation of Pu_2O_3 has been estimated by Roberts:[18]

$$\Delta H^\circ_{298} = -393{,}000 \pm 10{,}000 \text{ cal/mole}$$

The abnormal cubic Pu_2O_3 may be made by heating the dioxide in vacuo at 1650 - 1800°.[19] It is semi-metallic in nature and apparently of variable composition, the upper-limit possibly being Pu_4O_7.[20]

2-2.3 Higher Oxides of Plutonium. Brewer's[21] prediction that solid plutonium oxides higher than PuO_2 would not be thermodynamically stable has so far been sustained. Efforts to produce a higher oxide by reacting PuO_2 with ozone at 800 and 1000°,[19] 70 atmospheres pressure of oxygen at 400°,[22] atomic oxygen,[22] and NO_2 at 500°[23] were unsuccessful, although, as discussed above, plutonium dioxide with O/Pu ratios greater than 2.00 often results from low-temperature ignition of plutonium compounds. Oxygen-rich PuO_2 can also be produced by heating cubic Pu_2O_3 in oxygen at 1000°. The PuO_2 thus formed has reduced lattice parameters, i.e., 5.3820 A as compared to 5.3960 A for the stoichiometric plutonium dioxide. The excess oxygen is apparently accommodated in the interstices of the plutonium dioxide lattice, and the resulting compound is not at all analogous to the higher oxides produced by the oxidation of uranium dioxide.

2-3 PLUTONIUM PEROXIDE AND HYDROXIDES

Because of its process importance, plutonium peroxide has been investigated in great detail. Even if it were not of current utility, the uniqueness of the peroxide would make it an interesting compound for study.

2-3.1 Plutonium Peroxide. Plutonium peroxide is formed by precipitation from aqueous solution with hydrogen peroxide (usually of 30 per cent concentration). The precipitation is best done at reduced temperature (10 - 15°) and from a solution no more than 5 normal in acid concentration in order to avoid decomposition of the peroxide. First the hydrogen peroxide converts all plutonium ions to the IV state; normally about one hour should be allowed for this reaction to be completed in the absence of a significant concentration of plutonium (IV). Further addition of hydrogen peroxide produces a brown complex, consisting of two plutonium atoms, two peroxy-oxygen atoms, and one hydroxide group;[24] this is converted to a red complex containing two plutonium atoms and four peroxy-oxygen atoms as more peroxide is added. (Peroxide complexes of plutonium are discussed in Sec. 3-3.2.7.) Addition of still more hydrogen peroxide causes precipitation of green plutonium peroxide, which is digested at reduced temperature for about 30 minutes and then filtered through a medium-porosity sintered platinum filter.[25] The filtrate, which contains about 10 per cent excess hydrogen peroxide, may be decomposed in a controlled manner by allowing it to drip into a vessel containing sodium hydroxide pellets. The precipitate is then washed several times with 6 per cent hydrogen peroxide, then with absolute ethanol, and finally dried by pulling air through it.

The reduction of plutonyl (VI) to plutonium (IV) is very slow at the precipitation temperature;[25] if appreciable plutonyl (VI) is present in the solution, the digestion time must be increased (sometimes to several days) in

order to prevent high plutonium losses in the filtrate. Usually it is preferable to reduce the plutonium (VI) to the (IV) state with another reducing agent (but not Fe^{++}) before peroxide is added.

A high concentration of iron, which catalyzes the decomposition of peroxide, can cause an increase in filtrate losses of plutonium and also result in undesirable heat evolution during the precipitation.[24] Table 2.8 gives an indication of the effect of iron concentration on filtrate losses; presumably other ions that decompose peroxide, such as copper and manganese, would have a similar effect.

The peroxide is soluble in concentrated nitric acid, but dissolution must be undertaken carefully to prevent excessive foaming due to the large quantities of gas evolved. It is preferable to add the peroxide to the acid in small increments.

The chemical composition, as well as the crystal structure, of plutonium peroxide varies with the method of preparation. Hamaker and Koch[26] found that the peroxide always incorporated anions from the solution. Compositions obtained by precipitations from various acids are given in Table 2.9.

It will be noted that all of the precipitates contain sulfate, which is present as an impurity in the hydrogen peroxide and is held tenaciously by the precipitate.

Plutonium peroxide exists in two crystalline forms, as shown in Table 2.10. Although both the hexagonal and cubic forms are compounds of plutonium (IV), they have different $O^{=}$/Pu ratios. The hexagonal precipitate has an average $O^{=}$/Pu ratio of 3.37 when wet and 3.02 $\pm$ 0.07 after drying; the cubic form $O^{=}$/Pu ratio averages 3.03 $\pm$ 0.04, regardless of whether the precipitate is wet or dry.

The cubic precipitate is colloidal in nature and not suitable for process applications; therefore, conditions necessary for the preparation of the

Table 2.8 - EFFECT OF IRON CONCENTRATION ON PEROXIDE FILTRATE LOSSES[25]

Iron Concentration in Feed Solution, M	Plutonium Concentration in Filtrate, mg/liter
$<10^{-5}$	49
8.3×10^{-4}	65
4.1×10^{-3}	112
8.3×10^{-3}	160
8.3×10^{-2}	205

Table 2.9 - COMPOSITIONS OF PLUTONIUM PEROXIDE PRECIPITATED FROM VARIOUS ACID SOLUTIONS[26]

Acid	Peroxide Composition
Sulfuric Acid	$Pu(O^-)_{2.68-2.85}(SO_4^=)_{0.32-0.33}(NO_3^-)_{0.00-0.04}(O^=)_{0.24-0.34} \cdot (2.06-2.68)H_2O$
Nitric Acid	$Pu(O^-)_{2.61-3.52}(SO_4^=)_{0.05-0.14}(NO_3^-)_{0.06-0.33}(O^=)_{0.06-0.46} \cdot (1.65-2.68)H_2O$
Hydrochloric Acid	$Pu(O^-)^*_{2.24-2.54}(SO_4^=)_{0.02}(Cl^-)_{0.45-0.47}(O^=)_{0.48-0.63} \cdot (3.0-3.1)H_2O$

*Peroxide oxygen in this compound may be low due to possible decomposition.

Table 2.10 - CRYSTAL STRUCTURE DATA FOR PLUTONIUM PEROXIDE

Structure	Lattice Constant, A[26]	Tamp Density,[25] g/cm^3	Particle Density,[25] g/cm^3
Hexagonal	a = 4.00	0.17	3.43
Face-Centered Cubic	a = 16.5	0.70	3.71

preferred hexagonal form have been determined. The acidity of the solution has a definite influence on the structure: in general, the cubic precipitate results when precipitation occurs from solutions with less than two molar acidity. Table 2.11 lists data on the variation of structure with acidity for nitric, hydrochloric, perchloric, and sulfuric acid solutions.

The structure of the precipitate apparently is independent of sulfate concentration, and of concentration of hydrogen peroxide between one and three molar, but seems to be influenced by the perchlorate concentration. Thus, at constant acidity, increasing the perchlorate concentration from 0.25 to 4.0 molar caused the structure to change from cubic to hexagonal; no perchlorate ion was detected in the precipitates, however.

Processes employing plutonium peroxide are discussed in Sec. IV, Chap. 2, Sec. 2-1.1.

2-3.2 Plutonium Hydroxides. The hydroxides (or probably more accurately, the hydrous oxides) of plutonium are gelatinous materials of variable and somewhat uncertain composition. The formulas given for them below should be considered as only approximate. Plutonium hydrolysis and polymer formation are discussed in Chap. 3, Sec. 3-2.

2-3.2.1 Plutonium (III) Hydroxide. Plutonium (III) hydroxide, $Pu(OH)_3 \cdot x\ H_2O$, apparently precipitates from alkaline solutions of plutonium (III).[21] The blue precipitate is rapidly oxidized by air to plutonium (IV) hydroxide. Its solubility product has been extimated as 2×10^{-20}.[27]

2-3.2.2 Plutonium (IV) Hydroxide. Addition of hydroxide to a plutonium (IV) solution produces a green gelatinous precipitate of plutonium (IV) hydroxide, $Pu(OH)_4 \cdot x\ H_2O$, that is difficult to filter. It may be dried by gentle heating at 70 - 100°; at higher temperatures it is converted to the dioxide.

Table 2.11 - EFFECT OF ACIDITY ON CRYSTAL STRUCTURE OF PLUTONIUM PEROXIDE PRECIPITATE[25]

Pu	Concentration, moles/liter H_2O_2	H^+	NO_3^-	Cl^-	ClO_4^-	$SO_4^=$	Structure
0.003	3.00	0.45	3.0		0.25		Cubic
0.033	3.00	1.0	3.0		0.25		Mixture
0.033	3.00	2.0	3.0		0.25		Hex.
0.033	3.00	3.2	3.0		0.25		Hex.
0.053	1.00	0.51		3.0			Cubic
0.053	1.00	2.8		3.0			Cubic
0.053	1.00	3.6		3.8			Hex.
0.176	3.30	1.10			1.60		Cubic
0.229	1.35	1.44			2.12		Cubic
0.264	0.25	4.10			4.63		Hex.
0.176	3.30	4.10			4.63		Hex.
0.033	1.00	0.55				0.37	Cubic
0.033	3.00	4.0				2.0	Hex.
0.176	3.00	4.2			0.53	2.0	Hex.

Plutonium (IV) hydroxide is soluble in dilute acids, although at least four equivalents of hydrogen ion must be used per mole of plutonium to prevent formation of an acid-insoluble polymer.[28]

Because of the nonselectivity of hydroxide precipitations, this compound has no utility as a means of plutonium purification; it has been used extensively, however, to remove plutonium from waste solutions because of its extremely low solubility product: $[Pu^{4+}][OH^-]^4 = 7 \times 10^{-56}$.[29]

Further discussion of the formation of plutonium hydroxides and polymers will be found in Chap. 3, Sec. 3-2.

2-4 PLUTONIUM FLUORIDES

Plutonium forms fluorides in the (III), (IV), and (VI) oxidation states; there are at present no known plutonium (V) fluorides. Thermodynamic and X-ray data for the fluorides are given in Table 2.12. All of the fluorides are of great interest and will be discussed in detail.

2-4.1 Plutonium (III) Fluoride. Plutonium trifluoride may be prepared by several methods:

1. Anhydrous plutonium trifluoride results from the treatment of plutonium (IV) nitrate, oxide, hydroxide, peroxide, fluoride, oxalate, plutonium (III) oxalate, or plutonyl (VI) nitrate with anhydrous hydrogen fluoride at 550 - 600°.[38] Reaction time varies; for the (III) oxalate it is about four hours.[39] Although commercial hydrogen fluoride contains small amounts of reducing impurities that favor formation of the trifluoride, it is advisable to add a small quantity (approximately one percent) of hydrogen to assure that none of the tetrafluoride will be formed. The reaction may be carried out in equipment such as that illustrated in Fig. III.1. Although fluorination of plutonium (IV) oxalate can proceed directly without formation of an oxide intermediate, Myers[40] recommends calcining at 480° to the dioxide, which is then fluorinated. The latter reaction takes place according to the equation:

$$PuO_2 + 3HF + 1/2H_2 \longrightarrow PuF_3 + 2H_2O$$

2. Reaction of dichlorodifluoromethane with plutonium (III) or (IV) oxalate produces the trifluoride.[41] The oxide may also be used as starting material, in which case the reaction proceeds as follows:[42]

$$2PuO_2 + 3CCl_2F_2 \longrightarrow 2PuF_3 + CO_2 + 2COCl_2 + Cl_2.$$

When the oxalate is used, it is decomposed to the dioxide, which then reacts according to the above equation. This procedure produces trifluoride

Table 2.12 - THERMODYNAMIC AND X-RAY/DATA FOR THE FLUORIDES OF PLUTONIUM*

-ΔH, kcal/mole	Melting Point, °C	Symmetry	Space Group	Lattice Parameters, A a_o	b_o	c_o	Formula Units per Unit Cell	Calculated Density, g/cm³
375	1425	Hexagonal	-	4.095±0.001	-	7.254±0.001	2	9.32
-	>1635	Face-centered cubic	-	5.71±0.01	-	-	-	9.76
-	-	Hexagonal	C32	6.13±0.02	-	3.76±0.01	1.5	6.87
424	1037	Monoclinic	C2/c	12.62±0.06	10.57±0.05 $\alpha = 126^{\circ}10' \pm 30'$	8.28±0.05	12	7.0
-	-	Pseudo-Cubic	-	≈5.64	-	-	-	-
-	-	Orthorhombic	Pnam	12.66±0.05	11.03±0.05	6.99±0.05	8	4.89
-	-	Rhombohedral	$R\bar{3}(C_{3i}^2)$	8.95±0.03	- $\alpha = 107^{\circ}28' \pm 10'$	-	6	6.03
		Pseudo-Cubic	(Pseudocell)	5.650±0.005	- $\alpha = 90^{\circ}$	-	-	-
-	-	Hexagonal	-	6.055±0.005	-	3.571±0.003	-	5.84
-	-	Rhombohedral	$R\bar{3}(C_{3i}^2)$	9.29±0.03	- $\alpha = 107^{\circ}2' \pm 10'$	-	6	5.66
		Pseudo-Cubic	(Pseudocell)	5.86±0.01	- $\alpha = 89^{\circ}20'$	-	-	-
-	-	Rhombohedral	$R\bar{3}(C_{3i}^2)$	9.48±0.03	- $\alpha = 106^{\circ}56' \pm 10'$	-	6	5.88
		Pseudo-Cubic	(Pseudocell)	6.00±0.02	- $\alpha = 89^{\circ}10'$	-	-	-

CRYSTALLOGRAPHIC

Table 2.12 - THERMODYNAMIC AND X-RAY/DATA FOR THE FLUORIDES OF PLUTONIUM* (continued)

r	$-\Delta H$, kcal/mole	Melting Point, °C	Symmetry	Space Group	Lattice Parameters, A a_o	b_o	c_o	Formula Units per Unit Cell	Calculated Density, g/cm^3
	-	-	Orthorhombic	Pnam	8.58±0.04	6.96±0.04	11.35±0.06	4	6.73
own	-	51.59	Orthorhombic	Oh	-	-	-	-	-
	-	-	Rhombohedral	-	5.797±0.005	- $\alpha = 42^o \pm 3'$	-	-	6.50

*Table compiled in part by Katz and Seaborg[30] from data of Cunningham[31] and Zachariasen[32, 33, 34, 35, 36]

Additional information added from References 37, 62, 73, and 74.

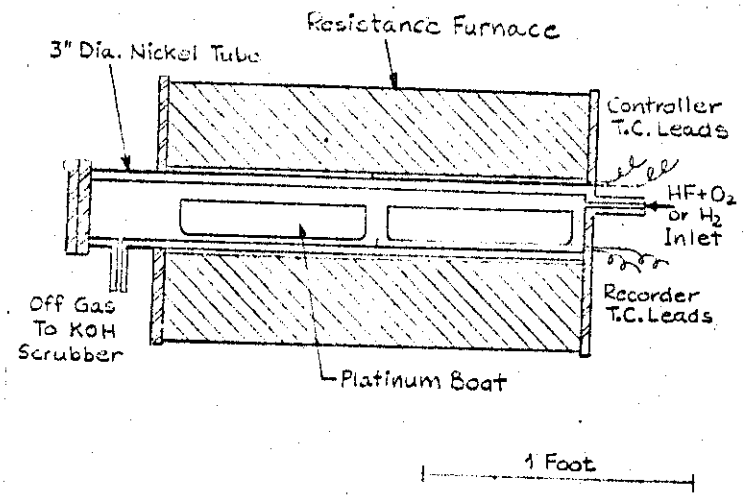

Fig. III.1 - Furnace and reaction tube for preparation of plutonium fluorides.

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with a higher bulk density than that obtained by fluorination; it has the further advantage of using relatively noncorrosive materials.[41]

3. Addition of aqueous hydrofluoric acid to a solution of plutonium ((III) (prepared by reducing ions of higher valence with hydroxylamine or ascorbic acid) in nitric or hydrochloric acids precipitates the trifluoride, which may then be filtered, washed with dilute hydrofluoric acid and acetone, and dried by pulling air through the cake. The resulting plutonium trifluoride is not anhydrous, as shown below.

Dawson and Elliott[43] have made a thermogravimetric study of plutonium trifluoride samples prepared under various conditions. From the weight change observed in each case when the sample was ignited to plutonium dioxide, they were able to calculate the molecular weight (and therefore the degree of hydration) of the original trifluoride. Also from the shapes of the weight-versus-temperature curves it was possible to determine the temperatures necessary to dehydrate trifluoride samples of each particular preparative history. The thermogravimetric curves they obtained are reproduced in Fig. III.2.[43]

The curve for plutonium trifluoride produced by fluorination of the dioxide [obtained by calcining plutonium (IV) oxalate (Fig. III.2)] reveals that this trifluoride is anhydrous. It is stable in air up to about 300°; at that point it begins to react with moisture in the air. Conversion to plutonium dioxide is not complete until a temperature of approximately 650° is reached. The trough observed at 500 - 600° on this and the subsequent curves is thought to be due to a region of apparent stability of an oxide with an O/Pu ratio less than 2.0 (1.86-1.91). Efforts to isolate this material were unsuccessful.[43]

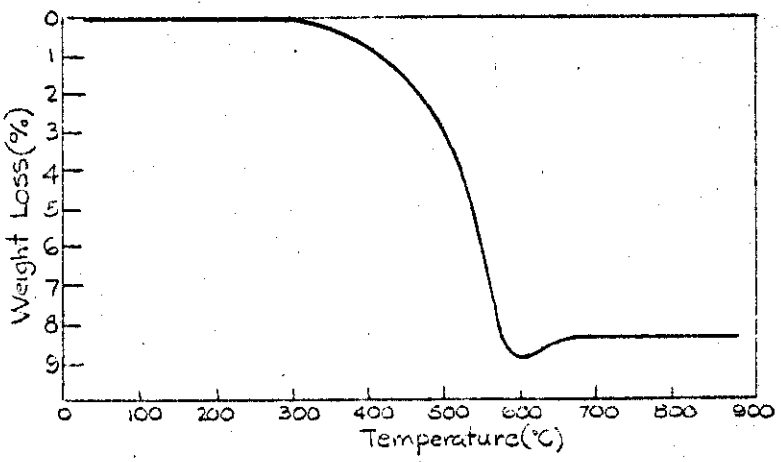

Fig. III.2 - Thermogravimetric curve for plutonium trifluoride freshly-prepared by fluorination.[43]

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Plutonium trifluoride made by fluorination and exposed to air for 12 days produced the thermogravimetric curve shown in Fig. III.3. The weight change indicates that 0.61 per cent moisture was adsorbed, but that it was removed by heating to about 100°. Conversion of this material to the dioxide occurrs at a temperature approximately 100° lower than that for the dry plutonium trifluoride represented in Fig. III.2.

Plutonium trifluoride precipitated from aqueous solution is hydrated. It cannot be dehydrated by heating in air, as is evident in Fig. III.4; raising the temperature merely causes a gradual and fairly linear weight loss until conversion to plutonium dioxide is complete at about 550°. The weight loss indicates that the precipitated trifluoride has approximately the composition $4PuF_3 \cdot 3H_2O$. The X-ray diffraction pattern, although diffuse, appeared to be the same as that of the anhydrous compound, thus making it seem unlikely that the water is incorporated into the lattice. It was suggested that the water may be trapped between layers of fluorine atoms at the time of precipitation; the variations in X-ray pattern resulting would be obscured by the diffuseness of the film. Plutonium trifluoride precipitated at 80° contained less water.

Anhydrous plutonium trifluoride is difficult to prepare by heating the hydrated material in air; if, however, $4PuF_3 \cdot 3H_2O$ is heated in hydrogen fluoride-hydrogen at 500°, vacuum to 300°,[43] or in helium at 600° for 30 minutes,[44] the anhydrous trifluoride is formed. In the latter case the trifluoride produced has less than 0.2 percent water. The dehydration is irreversible; anhydrous trifluoride prepared in this manner did not absorb water when stored under aqueous hydrofluoric acid for several days.[43]

Plutonium trifluoride, a bluish-violet compound, is quite insoluble in acids in the absence of strong fluoride-complexing cations (such as

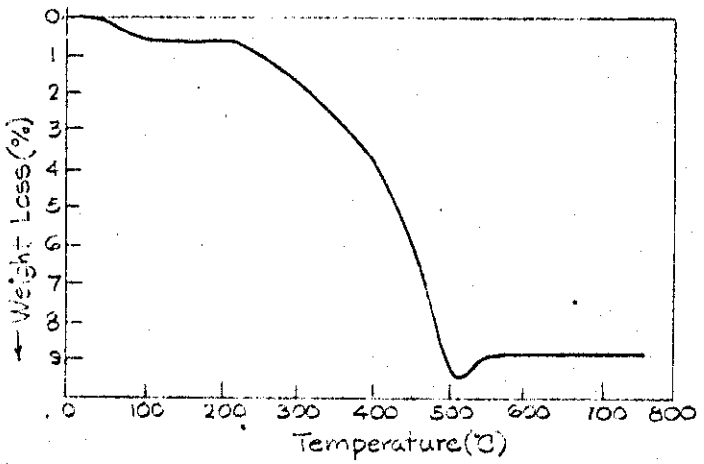

Fig. III.3 - Thermogravimetric curve for plutonium trifluoride prepared by fluorination after standing in laboratory air for 12 days.[43]

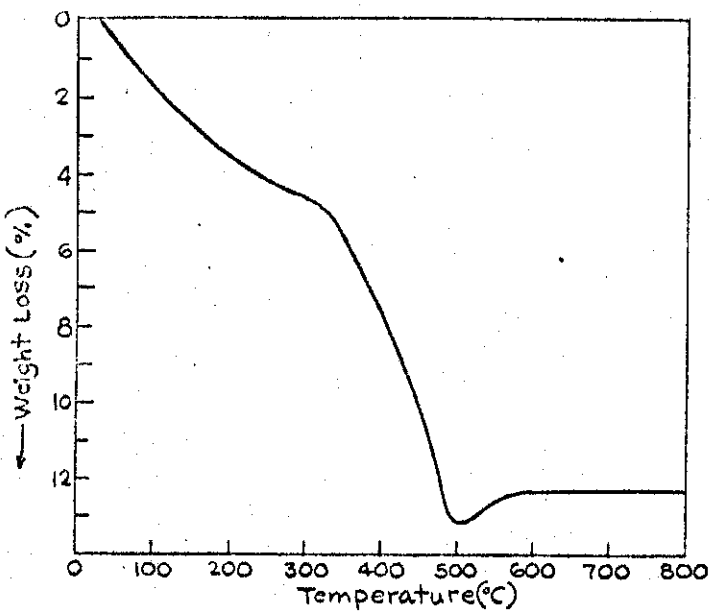

Fig. III.4 - Thermogravimetric curve for precipitated plutonium trifluoride.[43]

aluminum and zirconium). Its solubility in one molar hydrofluoric acid - one molar hydrochloric acid for example, is about 37 milligrams per liter.[44] The bulk density of the dried trifluoride precipitate varies from 1 - 2.5 grams per cubic centimeter.

Mandleberg, Francis, and Smith[45] have determined the solubility of plutonium trifluoride in nitric-hydrofluoric acid mixtures at 25°. Their values were obtained by two methods:

1. By adding hydrofluoric acid to solutions of plutonium trifluoride in nitric acid of known concentration and agitating precipitate and supernate for 15 - 18 hours;

2. By stirring excess solid plutonium trifluoride with acid mixtures of the appropriate concentrations for 15 - 18 hours.

In both cases the concentration of plutonium in the supernatant was determined by counting techniques. The values obtained by both methods are given in Table 2.13.

Agitation times were probably too short for equilibrium to be reached, so the above values may best be considered "practical" solubilities, i.e., solubilities likely to be achieved under plant operating conditions, rather than as equilibrium values.

It will be noted that increasing the hydrogen fluoride concentration at concentrations above about two molar does not appreciably decrease the solubility of the trifluoride. This effect is probably due to the low dissociation of hydrogen fluoride, such that addition of acid above two molar does not materially alter the fluoride ion concentration.

From the above data the mean solubility product of plutonium trifluoride has been calculated:

$$[Pu^{3+}][F^-]^3 = K_{S.P.} = 2.5 \times 10^{-16}$$

Table 2.13 - SOLUBILITY OF PLUTONIUM TRIFLUORIDE IN NITRIC-HYDROFLUORIC ACID MIXTURES AT 25°[45]

HNO_3 Conc., M	HF Conc., M	Solubility, g Pu(III)/liter
0.05	0.00	0.157
	0.54	0.080
	0.96	0.067
	1.65	0.049
	2.5	0.038
	3.9	0.039
	6.07	0.041
	7.45	0.044
0.16	0.00	0.202
	0.52	0.137
	1.00	0.082
	1.68	0.064
	3.3	0.057
	4.94	0.046
	6.84	0.037
	7.94	0.024
0.30	0.00	0.955
	0.59	0.068
	1.33	0.049
	2.09	0.050
0.61	0.00	1.710
	0.57	0.233
	1.07	0.074
	2.01	0.058
	3.07	0.070
1.15	0.3	0.084*
	0.8	0.047*
	1.25	0.040*
	1.65	0.014*
1.20	0.00	2.691
	0.57	0.319
	1.17	0.102
	1.73	0.088
	2.37	0.065
	3.97	0.053
	6.87	0.048
2.25	0.3	0.073*
	0.7	0.053*
	1.15	0.038*
	1.55	0.019*
	3.00	0.055*
	4.35	0.59*
2.40	0.00	4.589
	0.35	0.141
	0.65	0.097
	2.31	0.064

*Values obtained by Method 2; all others obtained by Method 1.

The above value was calculated with the assumption that the free fluoride ion concentration will be negligible compared to the hydrogen fluoride concentrations, and that the latter may be considered equivalent to the dissolved fluoride concentration. This assumption is not valid below acidities around 0.1 molar, so the above solubility product is of dubious validity in this region. Also, since it was calculated from nonequilibrium data, the solubility product should be considered as only approximate in any acidity range. It is probably accurate to within one or two orders of magnitude, however.

The absorption spectrum of crystals of plutonium trifluoride in the 3,400 to 10,000 A range has been determined by Lipis and Pazharskii.[46] The spectrum is changed by the presence of water of crystallization, but not by adsorbed or occluded water.

From equilibrium constants for the distribution of plutonium between molten UF_4 and molten irradiated uranium metal, Buyers and Murbach[47] have calculated the free energy of formation of plutonium trifluoride at 1573°K:

$$\Delta F^{\circ}_{1573} = -279 \pm 4.5 \text{ kcal/mole.}$$

Glassner[48] has estimated the free energy of formation at 298°K:

$$\Delta F^{\circ}_{298} = -357.2 \text{ kcal/mole.}$$

Westrum and Wallmann[49] found the melting point of plutonium trifluoride to be 1425°±3° and the heat of sublimation to be 89 kcal/mole. They obtained the following equation for the vapor pressure of the trifluoride from 1200 to 1660°K:

$$\log_{10} P \text{ (mm Hg)} = -24{,}917/T - 7.5513 \log T + 38.920.$$

These values are somewhat at variance with the earlier values of Phipps et al.,[50] which were based on an incorrect melting point for plutonium trifluoride. The data of Phipps and co-workers,[50] however, fit the equation derived by Westrum and Wallman.[49] While the latter appears to be the best equation currently

available for calculating the vapor pressure of plutonium trifluoride, it should be regarded as tentative until it is put on a more firm experimental basis.

Plutonium oxyfluoride, PuOF, was identified by X-ray diffraction as one of the products of an attempted atomic hydrogen reduction of plutonium tetrafluoride.[51] It was also prepared inadvertently during an effort to determine the melting point of the trifluoride in an argon atmosphere.[52] Apparently only a very slight partial pressure of oxygen is required for its formation from the trifluoride.

One plutonium (III) fluoride double salt, $NaPuF_4$, has been reported.[34] It was prepared accidentally during an attempt to reduce the trifluoride with sodium vapor, and was identified by X-ray diffraction.

Process applications of plutonium trifluoride are discussed in Sec. IV, Chap. 2, Sec. 2-1.2.

2-4.2 Plutonium (IV) Fluorides. Plutonium tetrafluoride may be prepared by the fluorination of plutonium (IV) oxide, peroxide, hydroxide, nitrate, oxalate or plutonium (III) oxalate at 500 - 550° in the presence of oxygen. Reaction with the peroxide is vigorous initially; it is therefore necessary to add the hydrogen fluoride-oxygen slowly during the early stages of the reaction. The reaction with the dioxide may be represented by the equation:[65]

$$PuO_2 + 4HF + O_2 \xrightarrow{550^\circ} PuF_4 + 2H_2O + O_2$$

In the case of the oxalate, it has been demonstrated that direct fluorination can take place without formation of the dioxide as an intermediate;[53,54] Myers[40] states, however, that optimum production of the tetrafluoride calls for calcination of the oxalate at 480° followed by fluorination at 500°. The production of the tetrafluoride is similar to that of the trifluoride, with

the exception that oxygen, rather than hydrogen, is added to the hydrogen fluoride. The apparatus shown in Fig. III.1 may be used for the preparation of plutonium tetrafluoride.

Plutonium tetrafluoride prepared by the above method is stable in moist air up to about 300°;[43] at this point it begins to form the dioxide, the conversion being complete at around 600°. A sample allowed to stand in air for two days adsorbed about 0.6 percent moisture, which was easily driven off by heating to 50°.

The reaction of sulfur tetrafluoride with plutonium dioxide at 600° has been reported to give plutonium tetrafluoride in 45 percent yield after one hour, according to the following equation:[55]

$$PuO_2 + 2SF_4 \rightarrow PuF_4 + 2SOF_2$$

The reaction rate is significant only at temperatures above 450°.

The tetrafluoride may be formed by fluorinating the trifluoride in the presence of oxygen at 500°:

$$PuF_3 + HF + 1/4O_2 \rightarrow PuF_4 + 1/2H_2O.$$

Precipitation of plutonium (IV) from aqueous solution gives the hydrate $PuF_4 \cdot 2.5H_2O$.[54] Vacuum dehydration of this material at 200° yields $PuF_4 \cdot H_2O$; further heating results in the trifluoride, presumably due to the following net reaction,[54] the equilibrium being displaced to the right in vacuum:

$$4PuF_4 + 2H_2O \rightarrow 4PuF_3 + 4HF + O_2$$

Anhydrous plutonium tetrafluoride has been prepared, however, by slowly heating $PuF_4 \cdot 2.5H_2O$ to 600° in a sufficiently fast flow of inert gas to remove the water as soon as it is evolved.[56]

Plutonium tetrafluoride is one of the products of the reaction of dry oxygen with the trifluoride:[57]

$$4PuF_3 + O_2 \underset{\text{vacuum}}{\overset{600^\circ C}{\rightleftharpoons}} 3PuF_4 + PuO_2$$

From the pressures of oxygen evolved at various temperatures by means of the reverse reaction, Dawson et al.[58] calculated the values for the free energy of formation of PuF_4 shown in Table 2.14.

Mandleberg and Davies[59] have measured the vapor pressure of plutonium tetrafluoride by means of an effusion technique. At temperatures between 700 and 1200°C, the vapor pressure may be represented by the following equation:

$$\log_{10} P(\text{mm Hg}) = 5.58 - 10{,}040/T(^{\circ}K).$$

Above 1200° the vapor pressure increases much more rapidly with temperature, probably due to formation of PuF_5 by the following reaction:

$$2PuF_4 \longrightarrow PuF_5 + PuF_3.$$

Since the vapor pressure of plutonium trifluoride at these temperatures is lower than that of the tetrafluoride, the increase in pressure is believed to be due to the volatility of PuF_5. Above 1200° the vapor pressure is represented by the equation:

$$\log_{10} P(\text{mm Hg}) = 36.1 - 54{,}180/T(^{\circ}K).$$

The probable formation of volatile plutonium pentafluoride by the high-temperature disproportionation of the tetrafluoride was confirmed by Dawson and co-workers.[54]

The vapor pressure of plutonium tetrafluoride has been determined by Berger and Gaumann[60] by heating a small sample in vacuo at various temperatures and obtaining the weight and fluorine analysis of the sublimate condensed on a cold finger (cooled by liquid nitrogen) suspended a short distance above the sample. Their results indicated that in the temperature range 700 - 1000°, plutonium tetrafluoride is indeed the only sublimed species, and therefore partially confirmed the conclusions of Mandleberg and Davies. The vapor pressure expression obtained from their data, however, yields values that are higher (by factors up to ten) than those obtained by use of the Mandleberg

Table 2.14 - FREE ENERGY OF FORMATION OF PLUTONIUM TETRAFLUORIDE[58]

Temperature, °K	$-\Delta F^{\circ}$, kcal/mole
298	400
500	387
1000	353.5

and Davies equation. Agreement is fairly good when it is considered that the equations were derived from least-squares plots of data obtained by two different experimental techniques. While neither expression should be considered precise, it is probable that the equation of Mandleberg and Davies, which is based on a larger body of experimental data, is the more reliable.

Chudinov and Choporov[61] also obtained vapor pressure data for plutonium tetrafluoride by means of a modified Knudsen effusion method. From these values they calculated the heat and entropy of sublimation of the tetrafluoride to be 65.0 kcal/mole and 46.2 cal/mole degree respectively, in the temperature range from 500 to 850° .

Mandleberg, Francis, and Smith[45] determined the solubility of plutonium tetrafluoride in various concentrations of nitric acid by agitating mixtures of acid with an excess of the solid tetrafluoride. In each case duplicates were run and mixing was continued until equilibrium was attained; the values shown in Table 2.15 are therefore true equilibrium solubilities.

Comparison of these results with those for plutonium trifluoride in Table 2.13 reveals that at nitric acid concentrations above about 0.4 molar the tetrafluoride is appreciably more soluble than the trifluoride; in three molar nitric acid plutonium tetrafluoride is approximately twice as soluble as the trifluoride.

The above data have been used to calculate the mean solubility product for plutonium tetrafluoride:

$$[Pu^{4+}][F^-]^4 = K_{S.P.} = 6 \times 10^{-20}.$$

As in the case of the trifluoride, this value is based on the assumption that free fluoride concentration is negligible compared to hydrogen fluoride concentration, an assumption that is not true at acidities below about 0.1 molar. It is probably accurate to within an order of magnitude at higher acidities, however.

Table 2.15 - SOLUBILITY OF PLUTONIUM TETRAFLUORIDE IN NITRIC ACID AT 26.8°[45]

HNO_3 Conc., M	Solubility, g Pu(IV)/liter
0.0	0.060
0.015	0.088
0.15	0.460
0.30	0.820
0.59	2.24
0.74	2.90
1.00	4.19
1.59	5.8
3.19	10.4

A number of double salts of plutonium (IV) fluoride have been prepared by adding a metal fluoride, rather than hydrofluoric acid, to a plutonium (IV) solution. Thus Alenchikova and co-workers[62] prepared sodium-plutonium (IV) fluorides by the addition of excess sodium fluoride to a plutonium (IV) solution. A green precipitate formed, which gradually turned pink if allowed to remain under the supernatant liquid. Both fluorides were separated and dried at 85 - 90° and their compositions determined by means of X-ray, spectrophotometric, and chemical analyses. The green compound was found to be $NaPuF_5$ while the pink one proved to be Na_2PuF_6.

Addition of excess ammonium fluoride to a plutonium (IV) solution produced a mixture of green and pink precipitates, the green rapidly changing to pink.[62] The pink precipitate was identified as $(NH_4)_2PuF_6$. The green compound, while not analyzed, was thought to be $(NH_4)PuF_5$.

In a similar manner, green $KPuF_5$ and $RbPuF_5$ were precipitated by addition of the respective fluorides to plutonium (IV) solutions.[62] These stood in contact with their supernatant liquids several weeks before there was appreciable conversion to the pink forms, which were undoubtedly K_2PuF_6 and Rb_2PuF_6. Addition of cesium fluoride to a solution of tetravalent plutonium produced a red-brown precipitate that was not isostructural with the double fluorides of the other alkali metals.[62] It was found to be $CsPu_2F_9 \cdot 3H_2O$.

Powdered low-temperature plutonium dioxide and ammonium bifluoride, when intimately mixed, react exothermically at 50° to produce the pink double salt, NH_4PuF_5:[63]

$$2PuO_2 + 5NH_4F \cdot HF \longrightarrow 2NH_4PuF_5 + 4H_2O + 3NH_3$$

Upon heating to 300°, the double salt is rapidly decomposed to PuF_4.

Rapid addition of hydrofluoric acid to a nitrate solution containing equimolar concentrations of plutonium (IV) (40 - 65 g/l) and calcium precipitates

the double salt $CaPuF_6 \cdot nH_2O$.[64] Drying at 300° in argon produces the anhydrous salt. The solubility of this compound as a function of nitric and hydrofluoric acid concentrations is given in Table 2.16.[64]

Plutonium (IV) fluorides will be discussed in relation to chemical processing in Sec. IV, Chap. 2, Sec. 2-1.

2-4.3 Plutonium (VI) Fluorides. Volatile plutonium hexafluoride, PuF_6, may be prepared by reaction of the tetrafluoride with a stream of fluorine at elevated temperature:

$$PuF_4(s) + F_2(g) \rightarrow PuF_6(g) \qquad \Delta F^\circ_{298} = +6.5 \text{ kcal/mole}$$

The reaction proceeds at a satisfactory rate at 550°;[66] Weinstock and Malm[67] observed that the reaction can be completed in a matter of minutes at 750°. Florin et al.[68] fluorinated at 700°. The reaction may be accomplished in a tube furnace similar to that illustrated in Fig. III.1, with all metal parts in contact with PuF_6 being constructed of nickel or Monel, and all gaskets and valve packings made of Teflon. After reaction with plutonium tetrafluoride, the gas stream is immediately passed through a trap cooled by dry ice and trichloroethylene, which condenses the hexafluoride but not the fluorine.[66]

An alternate fluorination furnace utilizes induction heating.[67] The induction coil is cooled by liquid nitrogen to cause the plutonium hexafluoride to condense onto it as soon as formed. The pressure of fluorine is kept at 300 mm, the vapor pressure of liquid fluorine at liquid nitrogen temperature.

Plutonium hexafluoride can also be prepared by the fluorination of the dioxide.[69] The reaction could follow one of two possible paths:

$$PuO_2 + 3F_2 \rightarrow PuF_6 + O_2$$

or

$$PuO_2 + 2F_2 \rightarrow PuF_4 + O_2$$

followed by

$$PuF_4 + F_2 \rightarrow PuF_6$$

Table 2.16 - SOLUBILITY OF PLUTONIUM AS $CaPuF_6$ IN NITRIC-HYDROFLUORIC ACID MIXTURES[64]

	Plutonium solubility, g/liter								
	HNO_3 M								
HF M	1.0	1.4	2.0	3.0	4.0	6.0	8.0	10.0	11.0
1.0	0.34	0.60	0.71	0.16	0.38				
2.0	0.17	0.20	0.27	1.0	0.062	0.056	0.046	0.043	0.066
3.0	0.22	0.29	0.28	0.17	0.091				
4.0	0.33	0.24	0.28	0.16	0.12				
5.0	0.25	0.20	0.019	0.028	0.098				

Steindler and co-workers[69] found plutonium tetrafluoride in the residue from the fluorination of the dioxide and interpreted this to mean that the reaction follows the latter course, with the formation of the tetrafluoride as an intermediate.

It is of interest to note that plutonium hexafluoride cannot be prepared by the reaction of bromine trifluoride with plutonium tetrafluoride; plutonium hexafluoride is such a strong fluorinating agent that its converts BrF_3 to BrF_5.[67]

Plutonium hexafluoride, because of its high volatility, is the most hazardous of all plutonium compounds, and all work with it must be done with great care in absolutely leak-proof equipment.

It is normally stored in nickel or Monel containers. Pyrex and quartz equipment may be used for plutonium hexafluoride work if there is no hydrogen fluoride present; the latter reacts with these materials to form water, which then hydrolyzes the PuF_6.[67] The hydrogen fluoride may be removed by cooling the plutonium hexafluoride in a dry ice-trichloroethylene bath and pumping on it until the pressure is reduced to 10^{-5} mm of mercury. Occluded HF is removed by warming the hexafluoride slowly while pumping continues. Hexafluoride purified in this way has been stored in quartz and Pyrex containers for many months with no observable hydrolysis.[67]

The reaction of fluorine with plutonium tetrafluoride,

$$PuF_4(s) + F_2(g) \rightarrow PuF_6(g)$$

has been studied intensively. The rate has been found by Steindler et al.[69] to be dependent on the source of the tetrafluoride, probably due to particle size differences. The activation energy varies between 10 and 12 kcal/mole.

The equilibrium constant,

$$K = \frac{P_{PuF_6}}{P_{F_2}}$$

for the above reaction has been determined by Florin et al.,[68] Weinstock and Malm,[67] and Trevorrow and co-workers;[66] the latter data are considered the more reliable and will be discussed here. Trevorrow et al.[66] obtained the equilibrium values shown in Table 2.17.

From this table, it can be seen that the time required to reach equilibrium depends on the temperature: less than two hours at 300°, 24 - 60 hours at 200°, and 150 - 300 hours at 150°. These workers[66] also observed that the equilibrium constant did not vary with pressure in the range 900 - 6000 mm mercury.

The above results were plotted as log K vs. 1/T and fitted to a straight line by the least squares method to obtain an equation for the variation of equilibrium constant with temperature:[66]

$$\log_{10} K = -\frac{1331}{T(^{\circ}K)} - 0.275$$

An equation for the free energy of the reaction

$$PuF_4(s) + F_2(g) \rightarrow PuF_6(g)$$

from 150 - 400° was then derived:[66]

$$\Delta F^{\circ} = -RT\ln K = 6.09 \times 10^3 + 1.26T(^{\circ}K) \text{ cal/mole}$$

The mean value of ΔH° for the reaction was found to be $+6.09 \pm 0.14$ kcal/mole; from these values, ΔS° was calculated as -1.3 ± 0.2 cal/mole-degree.[66]

Plutonium hexafluoride is a solid with a melting point of 51.59°.[70] It is normally yellowish-brown in color, although the freshly-condensed material is frequently bright red. Unlike uranium hexafluoride, it has a liquid range at room temperature; the liquid is yellow in color. The vapor is brown in color, resembling nitrogen tetroxide. The vapor pressure has been determined from 0 to 77° by Weinstock, Weaver, and Malm[70] using a quartz sickle gauge. Their values, corrected for photochemical and radiation decomposition, are reproduced in Table 2.18.

Table 2.17 - EQUILIBRIUM DATA FOR THE REACTION $PuF_4(s) + F_2(g) \rightleftarrows PuF_6(g)$ [66]

Equilibrium Temperature, °C	Time at Equilibrium Temperature, hours	Equilibrium Constant, K, X10^4
395	2.5	50.5
393	3	55.6
336	17	33.5
342	18	37.9
302	1	26.4
303	2.5	26.5
301	1	28.8
302	3	24.5
301	2	25.6
302	2.5	28.0
300	24.5	26.6
251	18.5	16.4
251	66	15.1
199	25	7.08
202	24.5	6.19
200	23	8.18
200	47.5	6.67
152	136	4.68
150	312	4.55

Table 2.18 - VAPOR PRESSURE OF PLUTONIUM HEXAFLUORIDE [70]

Solid		Liquid	
Temperature, °C	Pressure, mm Hg	Temperature, °C	Pressure, mm Hg
- 0.01	17.9	52.02	543.6
6.21	28.8	55.17	597.8
10.27	38.0	57.29	650.3
10.76	40.2	62.06	760.6
14.73	52.3	63.09	777.8
15.10	52.9	66.16	866.9
19.30	70.5	69.85	972.1
19.75	71.7	71.29	1014.5
20.38	77.7	74.29	1111.1
23.12	90.0	77.16	1207.5
23.85	94.3		
27.73	128.1		
29.84	145.3		
32.51	173.2		
36.31	219.0		
39.58	266.1		
39.80	267.2		
42.61	318.0		
45.12	371.2		
45.84	381.9		
50.02	483.0		

The data fit the following vapor pressure equations:[70]

Solid PuF_6 (0° - 51.59°):

$$\log_{10} P(\text{mm Hg}) = -\frac{2095.0}{T(^\circ K)} + 3.4990 \log T(^\circ K) + 0.39024$$

Liquid PuF_6 (51.59° - 77.17°):

$$\log_{10} P(\text{mm Hg}) = -\frac{1807.5}{T(^\circ K)} - 1.5340 \log T(^\circ K) + 12.14545$$

From these equations the following physical properties of PuF_6 have been derived:

Boiling point:	62.16°
Triple point:	51.59° at 533.0 mm pressure
Heat of fusion:	4456 cal/mole
Entropy of fusion:	13.72 cal/mole-degree

The heats of sublimation and vaporation of plutonium hexafluoride have been plotted by Weinstock et al.[70] The heat of sublimation of the solid hexafluoride is approximately 11.5 kcal/mole and relatively insensitive to temperature variations up to the melting point, while the heat of vaporization of the liquid varies from approximately 7.15 kcal/mole at the melting point to about 6.85 kcal/mole at 77°.

The chemical properties of plutonium hexafluoride are greatly different from those of its uranium analogue. Plutonium hexafluoride, by virtue of being thermodynamically unstable (see above), decomposes more rapidly than the uranium compound, which has a negative free energy of formation. The net result is that PuF_6 is an excellent fluorinating agent; strong enough in fact to convert BrF_3 to BrF_5 and SF_4 to SF_6.[55] The equilibrium constant for the former reaction,

$$PuF_6 + BrF_3 \longrightarrow PuF_4 + BrF_5$$

has been calculated to be 1000 at 100°.[67] Plutonium hexafluoride can also be used to fluorinate uranium tetrafluoride to the hexafluoride, according to the following reactions:

$$4UF_4 + PuF_6 \rightarrow 2U_2F_9 + PuF_4$$

$$U_2F_9 + 1.5\ PuF_6 \rightarrow 2UF_6 + 1.5\ PuF_4$$

At 225°C the first reaction proceeds to completion, while the equilibrium constant for the latter reaction is greater than 10^7.[67]

Weinstock and Malm[67] found the molar magnetic susceptibility of plutonium hexafluoride at 81°K and 295°K to be 131 x 10^{-6} and 170 x 10^{-6} respectively. These workers also have studied the absorption spectrum of plutonium hexafluoride, with the results tabulated in Table 2.19.

Over the 5,000 - 25,000 A range the absorption spectrum consists of six groups of bands, each containing three or four bands of various intensities and separations of the order of 100 A. Apparently a vibrational spectrum is superimposed on the electronic transitions. The spectrum is being further investigated.[67]

Although plutonium hexafluoride is unstable with respect to dissociation into PuF_4 and F_2, the rate of attainment of equilibrium is so low at room temperature (see above) that it can be stored for fairly long periods of time without excessive decomposition. The equation for the decomposition of the hexafluoride is just the reverse of the equation for its formation, namely,

$$PuF_6 \rightarrow PuF_4 + F_2 \qquad \Delta F^\circ_{298} = -6.5 \text{ kcal/mole}$$

Trevorrow et al.[66] have demonstrated conclusively that the solid residue after decomposition is indeed PuF_4; previously there had been some suspicion that it might be Pu_4F_{17}. Fischer and co-workers[71] found that the rate of decomposition of PuF_6 is the result of simultaneous zero-order and first-order reactions:

Table 2.19 - FUNDAMENTAL VIBRATION FREQUENCIES OF PLUTONIUM HEXAFLUORIDE [67]

Designation	Symmetry Species	Spectral Activity	Frequencies, cm^{-1}
ν_1	A_{1_g}	Raman, p	628
γ_2	eg	Raman, dp	523
γ_3	f_{1_u}	Infrared	615*
γ_4	f_{1_u}	Infrared	203
γ_5	f_{2_g}	Raman, dp	211
γ_6	f_{2_u}	Inactive	171

*Only fundamental directly observed in the infrared.

$$-dp/dt = k_o + k_1 p$$

where

$$p = \text{pressure of } PuF_6$$

The zero-order expression is due to the heterogeneous decomposition of plutonium hexafluoride on the surface of plutonium tetrafluoride saturated with the gas; k_o, therefore, is dependent on the surface area of PuF_4 and varies with conditions. The first-order term describes the unimolecular, homogeneous decomposition of plutonium hexafluoride in the gas phase, and Fischer et al.[71] in their study found $k_1 = 2.50 \times 10^{-3}$ min.$^{-1}$ at 161°.

In addition to decomposition by the above processes, there is appreciable dissociation caused by α-radiation from the plutonium. The rate of radiation decomposition of solid plutonium hexafluoride was found by Weinstock and Malm[67] to be 1.5 percent per day; for the vapor, the rate varied from 0.06 to 0.35 percent per day, depending on the nature of the container.

While the absolute rate of decomposition of plutonium hexafluoride varies with conditions, representative values are of some interest. Over periods of several days, the average rate of decomposition of the hexafluoride has been found to be of the order of one percent per day or less, the rate decreasing with time.[72]

Plutonium hexafluoride is hydrolyzed by moist air to yield plutonyl (VI) fluoride, PuO_2F_2. The latter compound has also been prepared as a white precipitate[73] by treating plutonyl chloride solutions with hydrofluoric acid. Its solubility in water at 20° is reported as 1.07 grams per liter.

Plutonium hexafluoride is important in the fluoride volatility separations process, which is discussed in Sec. IV, Chap. 1, Sec. 1-4.1.

2-5 PLUTONIUM CHLORIDES, BROMIDES, IODIDES, AND IODATES

In contrast to the fluorides, plutonium chlorides, bromides, and iodides have found few important process applications, and have received relatively little study. Compounds of trivalent plutonium with chlorine, bromine, and iodine exist and have been characterized. To date, the only known plutonium (IV) compounds with these halogens are double chloride salts. Efforts to make all others have been unsuccessful. There are no known plutonium (V) halides, and plutonyl (VI) chloride is the only confirmed compound of plutonium (VI) with the higher halogens. Physical data on the higher halides and oxyhalides of plutonium are presented in Table 2.20.

2-5.1 Plutonium (III) Chlorides. Several methods are suitable for the preparation of plutonium trichloride:

1. The reaction of plutonium (III) oxalate with hexachloropropene at 180 - 190° for 18 hours yields plutonium trichloride of approximately 98 percent purity.[75] This procedure is the preferred method for the preparation of the trichloride.[39]

2. Plutonium trichloride may be prepared by direct combination of the elements.[76] This technique is rarely used currently.

3. Direct chlorination of plutonium metal may be used to prepare the trichloride. A smoother method is to start with plutonium hydride, prepared by reacting plutonium with hydrogen at 25 - 200°.[39] The hydride, which is placed on a Pyrex frit inside a Pyrex furnace tube, is heated to 450°, and hydrogen chloride gas is passed through it. Conversion to the trichloride is 99 percent complete after 12 - 15 hours. The product may be purified by filtration through sintered quartz or nickel filter discs, or by vacuum distillation at 900°.

4. Plutonium dioxide or oxalate may be converted to the trichloride by a number of chlorinating agents, among them phosphorus pentachloride at 280°,[76] sulfur dichloride at 800°,[76] hydrogen chloride-hydrogen at 700°,[76] phosgene at 400°,[79] and carbon tetrachloride at 450°,[79] the latter three being the most commonly used.

Plutonium (III) and (IV) oxalate produce the trichloride in quantitative yield when reacted with hydrogen chloride at 500° for four hours.[80] (A temperature of 550° gives a product with low chloride content.) It has been found desirable to heat the oxalate in a stream of argon for two hours at 140°, after which hydrogen chloride is substituted for argon, and the temperature raised quickly to 500°. Even when plutonium (IV) oxalate is the starting material, it is not necessary to use hydrogen, along with the hydrogen chloride, to reduce the plutonium (IV); presumably the reduction is effected by carbon monoxide formed by decomposition of the oxalate.

For chlorination, Tolley[79] prepared "reactive" plutonium dioxide by calcining plutonium (IV) oxalate at 300° for two hours. This material could then be reacted with phosgene at 350 - 400° for 1.5 hours to produce plutonium trichloride, while chlorination with carbon tetrachloride required four hours at 450° for completion.[79]

Boreham et al.[80] obtained complete conversion of plutonium (III) oxalate to the trichloride by phosgene in three to four hours at 600 - 650°, but the product was contaminated with carbon, possibly due to disproportionation of the carbon monoxide formed as a decomposition product of the oxalate. They were also able to produce the trichloride quantitatively by reacting phosgene for one to two hours at 400 - 500° with the "carbonate" precipitated by adding excess ammonium carbonate to a plutonium (III) solution in hydrochloric acid (See Sec. 2-6).

Table 2.20 - THERMODYNAMIC AND X-RAY DATA FOR PLUTONIUM CHLORIDES, BROMIDES, AND IODIDES*

	-ΔH, kcal/mole	Melting Point, °C	Symmetry	Space Group	Lattice Parameters, A a_o	b_o	c_o	Formula Units per Unit Cell	Calculated Density, g/cm^3
n	230.1	760	Hexagonal	$C6_3/m(C_{6h}^2)$	7.395±0.001	-	4.246±0.001	2	5.70
n	222.8	-	Tetragonal	$P4/nmm(D_{4h}^7)$	4.012±0.002	-	6.793±0.010	2	8.81
low	-	-	Hexagonal	$C\bar{3}m$	7.44±0.02	-	6.04±0.02	1	4.10
llow	-	-	Face-centered cubic	-	12.97	-	-	4	1.830
	-	-	Orthorhombic	Fmmm	14.2	14.5	13.5	4	-
yellow	-	-	-	-	-	-	-	-	-
	-	-	Tetragonal	$I/4m(C_{4h}^5)$	9.2	-	11.9	2	-
	-	-	Tetragonal	$I/4m(C_{4h}^5)$	10.0	-	12.9	2	-
n	187.8	681	Orthorhombic	$Ccmm(D_{2h}^{17})$	12.65±0.05	4.10±0.03	9.15±0.04	4	6.69
n	206	-	Tetragonal	$P4/nmm(D_{4h}^7)$	4.022±0.004	-	7.571±0.011	2	9.07
n	133	~777	Orthorhombic	$Ccmm(D_{2h}^{17})$	14.03±0.10	4.30±0.04	9.92±0.10	4	6.92
	183	-	Tetragonal	$P4/nmm(D_{4h}^7)$	4.042±0.002	-	9.169±0.015	2	8.46

e compiled in part by Katz and Seaborg[30] from data of Cunningham[31] and Zachariasen.[32,35,77,78]
tional information from References 88 and 91.

The reaction of plutonium dioxide with carbon tetrachloride at 700° has been studied by Budayev and Volsky.[81] The compositions of the solid and gaseous products of the reaction were determined, and the solid products even upon incomplete chlorination were found to consist only of plutonium trichloride and plutonium dioxide. The routes of the chlorination were postulated as follows:

$$PuO_2 + CCl_4 \rightarrow PuCl_3 + CO_2 + 1/2\ Cl_2$$

$$PuO_2 + 2CCl_4 \rightarrow PuCl_3 + 2CO + 2\ 1/2\ Cl_2$$

with only a slight contribution from the reaction:

$$PuO_2 + 2CCl_4 \rightarrow PuCl_3 + 2COCl_2 + 1/2\ Cl_2$$

Plutonium trichloride is a blue-to-green solid with a melting point of 760° and a boiling point of 1767°.[79] Tolley[79] found the free energy of formation at 25° to be -219 kcal/mole. Benz[82] determined the standard free energy of formation as a function of temperature to be

$$\Delta F_1^\circ = -221 + 0.05328T \text{ kcal/mole } (958 \text{ to } 1014^\circ K)$$

from potentiometric measurements in a galvanic cell containing fused $PuCl_3$ - KCl, (see Chap. 3, Sec. 3-6.2). By means of electromotive force measurements in fused $PuCl_3$ - NaCl, Benz and Leary[83] found the standard free energy and entropy of formation of pure solid plutonium trichloride at 700° to be -170 kcal/mole and -51.6 cal/mole-degree, respectively. Other thermodynamic data for plutonium trichloride are listed in Table 2.21.

Plutonium trichloride is deliquescent, and is very soluble in aqueous acid systems. The heat of solution of the trichloride in hydrochloric acid is shown in Table 2.22.

Martin and White[85] have determined the heat of solution of plutonium trichloride in perchloric acid-lithium perchlorate solutions. They compared their values with those quoted above to confirm the existence of trivalent plutonium chloride complexes.

Table 2.21 - THERMODYNAMIC DATA FOR PLUTONIUM TRICHLORIDE[50]

Vapor pressure (solid, 577° to melting point): $\log_{10} P\ (mm_{Hg}) = (12.726 \pm 0.126) - (15{,}910 \pm 120)/T(^\circ K)$

(liquid, to 977°): $\log_{10} P\ (mm_{Hg}) = (9.428 \pm 0.075) - (12{,}587 \pm 82)/T(^\circ K)$

ΔH of sublimation = 72.8±0.6 kcal/mole

ΔH of vaporization = 57.6±0.4 kcal/mole

ΔH of fusion = 15.2±0.7 kcal/mole

ΔS of fusion = 14.7±0.7 cal/mole-degree

Table 2.22 - HEAT OF SOLUTION OF PLUTONIUM TRICHLORIDE IN HYDROCHLORIC ACID AT 25°[84]

HCl M	-ΔH of Solution, kcal/mole $PuCl_3$
0.1	31.76
1.5	29.50
6.0	22.15
9.0	14.54

The spectrum of plutonium trichloride crystals in the 3,400 to 10,000 A wave length range has been determined by Lipis and Pozharskii[46] and found to be similar to that of an aqueous plutonium trichloride solution. The spectrum of the solid is altered by water of crystallization, but not by adsorbed or occluded water.

Blue-green plutonium oxychloride, PuOCl, has been prepared by reacting the trichloride at 650° with a gas mixture made by bubbling hydrogen through 38 percent hydrochloric acid at room temperature.[86] The product is insoluble in water but is soluble in dilute acids.

Several double salts of plutonium trichloride with potassium, rubidium, and cesium chlorides have been prepared in fused-salt systems; these compounds are described in Sec. 3-6.2.

2-5.2 Plutonium (IV) Chlorides. The only chlorides of plutonium (IV) known are complexes or double salts, the best known being cesium plutonium (IV) hexachloride, Cs_2PuCl_6, which was first prepared by Anderson[87] by the addition of cesium chloride solution to a solution of plutonium (IV) in hydrochloric acid. The solubility of Cs_2PuCl_6 is greatly dependent on hydrochloric acid concentration, as shown by Table 2.23.[89]

no ¶ In spite of its high solubility, cesium plutonium (IV) hexachloride has found application in plutonium electro lining processes under development.

By the use of analogous procedures, Anderson[87] also prepared the ditetramethylammonium compound, $[(CH_3)_4N]_2PuCl_6$, the dipyridinium salt, $(C_5H_5NH)_2PuCl_6$, and the diquinolinium compound $(C_9H_7NH)_2PuCl_6$; all have been verified by chemical analysis. Staritzky and Singer[88] prepared the tetramethyl compound $[(CH_3)_4N]_2PuCl_6$ as well as the tetraethyl salt, $[(C_2H_5)_4N]_2PuCl_6$, by the addition of 30 percent excess of the appropriate tetraalkylammonium chloride to a solution of plutonium (IV) in four molar hydrochloric acid and evaporating the solution under vacuum.

Table 2.23 - APPROXIMATE SOLUBILITY OF CESIUM PLUTONIUM (IV) HEXACHLORIDE IN HYDROCHLORIC ACID[89]

HCl M	Solubility, g./liter
4	171
5	80
6	41
7	17
8	8
9	5
10	4

While solid $PuCl_4$ apparently does not exist, Bagnall et al.[90] have prepared solid complexes of this compound with acetamide and N,N-dimethylacetamide. Addition, with stirring, of Cs_2PuCl_6 to a five-fold excess of acetamide in hot acetone or, preferably, cold ethyl alcohol, followed by filtering to remove the insoluble cesium chloride, produced a solution of the complex. The red-brown solid complex, $PuCl_4 \cdot 6CH_3CONH_2$, was then precipitated by the addition of isopentane or, less effectively, benzene or heptane, and recrystallized several times from ethanol. It was dried in a current of air and then at 10^{-3} millimeters pressure for several hours. The complex is soluble in hot acetone, methyl and ethyl alcohols, acetic acid and anhydride, but not in other organic solvents; it is hygroscopic, being readily decomposed by water. Upon heating, it loses acetamide continuously, with no evidence of an intermediate complex.

The N,N-dimethylacetamide complex, $PuCl_4 \cdot 2.5CH_3CON(CH_3)_2$, was prepared in a similar manner, except that acetone was used for recrystallization. It is more stable than the simple acetamide complex, and is not hygroscopic. The red-brown crystals melt at 171° to yield a dark red liquid. The complex is soluble in the same solvents as the acetamide derivative, and also in methylene chloride. Thermogravimetric studies indicated that there is a lower complex, $PuCl_4 \cdot 0.5CH_3CON(CH_3)_2$ stable in the 290 - 370° temperature range.

2-5.3 Plutonyl (VI) Chloride. Plutonyl chloride hexahydrate, $PuO_2Cl_2 \cdot 6H_2O$, has been prepared by the vacuum evaporation at room temperature of plutonyl (VI) chloride solutions,[91] the latter being prepared by the oxidation of plutonium (IV) solutions with chlorine. The identity of the greenish-yellow plutonyl chloride was confirmed by chemical and spectrophotometric analyses. The evaporation must be conducted on small quantities of solution and in very short time to prevent formation of tetravalent plutonium. Plutonyl

chloride is gradually decomposed on standing, probably due to α-radiation reduction of the plutonyl (VI).[91]

Staritzky and Singer[88] have prepared the tetramethyl and tetraethyl ammonium salts, $[(CH_3)_4N]_2PuO_2Cl_4$ and $[(C_2H_5)_4N]_2PuO_2Cl_4$, by adding the appropriate tetraalkylammonium chloride to a solution of plutonium (IV) in four molar hydrochloric acid and evaporating the solution under vacuum.

2-5.4 Plutonium (III) Bromides. Plutonium tribromide may be prepared by reactions somewhat analogous to those used for the preparation of the trichloride. Thus, it has been made by direct reaction of the elements at 400°, by treatment of plutonium dioxide or hydroxide with hydrogen bromide while heating to 800°, and by reacting the dioxide with a sulfur-bromine mixture at 800°.[92] Another method is that of Reavis and co-workers,[39] who reacted hydrogen bromide with plutonium hydride at 600°. At this temperature a partial removal of volatile impurities, such as ferric, aluminum, and zirconium bromides, was effected. The plutonium tribromide can be further purified by vacuum distillation at 900°.

Plutonium tribromide is a blue-green, deliquescent solid. Its vapor pressure has been determined as a function of temperature by Phipps and co-workers;[50] from these data they obtained the thermodynamic data listed in Table 2.24.

Lipis and Pozharskii[46] have determined the absorption spectrum of plutonium tribromide in the 3,400 to 10,000 A range, and found it to be similar to that of aqueous plutonium tribromide solutions. The spectrum of the solid is influenced by water of crystallization, but not by adsorbed or occluded water.

Plutonium oxybromide, PuOBr, has been made by reacting the dioxide at 750° with a gas mixture formed by bubbling hydrogen bromide through concentrated

Table 2.24 - THERMODYNAMIC DATA FOR PLUTONIUM TRIBROMIDE[50]

Vapor pressure (solid, 527° to melting point): $\log_{10} P\,(mm_{Hg}) = (13.386 \pm 0.077) - (15{,}280 \pm 69)/T(^{\circ}K)$

(liquid, to 827°): $\log_{10} P\,(mm_{Hg}) = (10.237 \pm 0.033) - (12{,}356 \pm 32)/T(^{\circ}K)$

ΔH of sublimation = 69.9±0.3 kcal/mole

ΔH of vaporization = 56.5±0.2 kcal/mole

ΔH of fusion = 13.4±0.3 kcal/mole

ΔS of fusion = 14.0±0.4 kcal/mole

(48 percent) hydrobromic acid at room temperature.[93] Although insoluble in water, it is soluble in dilute acids.[92]

2-5.5 Plutonium (III) Iodides. Plutonium triiodide has been prepared by reacting hydrogen iodide with plutonium metal at 450°.[94] The dioxide cannot be used as the starting material, since it is converted to plutonium oxyiodide. Presumably the triiodide could be prepared also by the action of hydrogen iodide on plutonium hydride.

Plutonium triiodide has a melting point of approximately 777°, and an estimated heat of fusion of 12 kcal/mole.[95]

Plutonium oxyiodide, PuOI, has been made by the action of a hydrogen iodide-hydrogen (20 - 40 mole percent) mixture on plutonium hydroxide.[94] It dissolves in dilute sulfuric acid, but is relatively insoluble in water.

2-5.6 Plutonium (III) Iodate. Plutonium triiodate, $Pu(IO_3)_3$, a tan solid, may be precipitated from trivalent plutonium solutions by the addition of an aqueous iodate solution (such as potassium iodate).[96] Its solubility in 0.017 molar potassium iodate - 0.17 molar sulfuric acid is 1.5 milligrams (as plutonium) per liter.

2-5.7 Plutonium (IV) Iodate. The pink tetraiodate of plutonium may be obtained as an amorphous precipitate from nitric acid solutions, as the data in Table 2.25 indicate.[97]

A thermogravimetric study by Dawson and Elliott[43] indicated that the precipitate has a molecular weight higher than $Pu(IO_3)_4$; the authors suggested that it may also contain iodic acid. The precipitate did not yield the pure tetraiodate on heating, but lost weight gradually to about 475 - 500°, at which point it decomposed rapidly to the dioxide.

Because of its low solubility even in moderately concentrated acid solutions, the tetraiodate has found application for analytical separations; its use for this purpose is currently minor, however.

Table 2.25 - SOLUBILITY OF PLUTONIUM TETRAIODATE IN POTASSIUM IODATE - NITRIC ACID SOLUTIONS[97]

KIO_3 M	Solubility, mg/liter HNO_3 M					
	1	2	3	4	5	6
0.1	3.7	5.4	6.6	13.7	46.5	94.5
0.15	1.6	2.1	2.5	6.9	16.5	24.9

2-6 PLUTONIUM CARBONATES AND OXALATES

These two classes of compounds, grouped together in the present discussion because of the general similarity of their anions, are nevertheless greatly different in their chemical and physical properties. In general the carbonates are rather ill-defined, unstable compounds, while the oxalates are well-characterized, stable compounds that are widely used as intermediates in the conversion of plutonium nitrate to metal (see Sec. IV, Chap. 2, Sec. 2-1.3 and 2-1.4).

2-6.1 Plutonium Carbonates. No solid carbonate compounds of plutonium (III) have been reported. Carbonates of plutonium (IV) and plutonyl (VI), and somewhat surprisingly, plutonyl (V), have been prepared and studied to some extent; in particular, the latter has received careful study by virtue of its uniqueness.

2-6.1.1 Plutonium (IV) Carbonates. Several complex ammonium-plutonium (IV) carbonates have been prepared by Gel'man and Zaitsev[98] by the hydrogen peroxide-reduction of plutonyl (VI) in ammonium carbonate solutions. The composition of the product was dependent on the concentration of the ammonium carbonate solution. Use of 20 percent ammonium carbonate solution formed the green compound $(NH_4)_6Pu(CO_3)_5 \cdot nH_2O$, which separated as a syrupy material when the solution was added to 75 - 80 percent alcohol or acetone. Attempts to dry the product in alcohol caused partial decomposition to a greenish-brown powder; decomposition was more rapid with air-drying, but was not complete, even after three months. After about six months, decomposition was complete, resulting in a green product that was essentially insoluble in water, but dissolved slowly in acids on heating. This compound was found by analysis to be $PuO_2 \cdot PuOCO_3 \cdot 3H_2O$. It had a refractive index slightly above 1.782, and its X-ray diffraction pattern revealed weak lines characteristic of PuO_2.

The thermal decomposition of $(NH_4)_6Pu(CO_3)_5 \cdot nH_2O$ was studied by differential thermal analysis. At 58 and 70°, loss of a molecule of ammonium carbonate and a partial loss of water, respectively, occurred with the formation of $(NH_4)_4Pu(CO_3)_4 \cdot 4H_2O$. This compound decomposed at 80° to yield $PuO_2 \cdot PuOCO_3$, which in turn decomposed to PuO_2 at 110°.

When the wet pentacarbonate compound was washed with 99 percent alcohol and dried in a desiccator over calcium chloride and ammonium carbonate for several days, partial decomposition to brown $(NH_4)_4Pu(CO_3)_4 \cdot 4H_2O$ took place. This compound decomposed in air in about three weeks to give a dark yellow powder that was insoluble in water and organic solvents, but soluble in acids with the evolution of carbon dioxide. Analysis indicated that this compound was apparently $PuOCO_3 \cdot 2H_2O$.

When plutonium carbonates were prepared in thirty percent ammonium carbonate (which, due to limited solubility, could be made only at 35° or above) the green compound $(NH_4)_8Pu(CO_3)_6 \cdot nH_2O$ was produced. It was found to be unstable in air and alcohol, decomposing in a manner similar to that of the pentacarbonate.

The ammonium plutonium (IV) tetracarbonate, pentacarbonate, and hexacarbonate are all readily soluble in water, but all decompose in aqueous solution in about twenty minutes, forming a green amorphous precipitate of plutonium hydroxide. Even so, it was possible to measure the molar conductance of $(NH_4)_4Pu(CO_3)_4 \cdot 4H_2O$ and also to determine its molecular weight by freezing-point lowering; these results indicated that the compound dissociates into five ions in aqueous solution. All three compounds may be kept in concentrated ammonium carbonate solutions for several days with no visible decomposition.

When aqueous solutions of the three carbonates were heated, the decomposition product was not plutonium hydroxide, but was a bright-green powder whose

analysis suggested it to be 2.5 $PuO_2 \cdot PuOCO_3 \cdot nH_2O$. The quantity of water was found to vary (averaging about 5.5), indicating that it did not exist as water of crystallization. Attempts to prepare the simple carbonate, $Pu(CO_3)_2 \cdot nH_2O$ by means of the reaction

$$(NH_4)_6Pu(CO_3)_5 \cdot nH_2O + 6HCl \rightarrow Pu(CO_3)_2 + 6NH_4Cl + 3CO_2 + nH_2O$$

failed; addition of hydrochloric acid precipitated $PuO_2 \cdot PuOCO_3$ instead.

It was not possible to prepare any higher ammonium plutonium (IV) carbonates because of the limited solubility of ammonium carbonate. This difficulty has been partially overcome in the preparation of the potassium plutonium (IV) carbonates, where $K_4Pu(CO_3)_4 \cdot nH_2O$, $K_6Pu(CO_3)_5 \cdot (3\text{-}4)H_2O$, and $K_8Pu(CO_3)_6 \cdot nH_2O$, as well as a higher compound, $K_{12}Pu(CO_3)_8 \cdot nH_2O$, have been prepared.[99]

2-6.1.2 Plutonyl (V) Carbonates. Solid double alkali carbonates containing plutonyl (V) as the PuO_2^+ ion have been precipitated by Nigon et al.[100] by the addition of solid alkali carbonate (to pH ~7) to a plutonyl (V) solution made by reduction of plutonyl (VI) with iodide ion. (The iodine was removed from the solution by extraction with carbon tetrachloride). The crystal structure of the product was found to be dependent on the alkali carbonate used: the predominant phase was hexagonal in the case of the ammonium salt and monoclinic for the sodium salt. The potassium salt prepared at a pH of about seven was hexagonal; at higher pH the orthorhombic form precipitated. Only the hexagonal form has been characterized. Ellinger and Zachariasen[101] have obtained the X-ray crystallographic data given in Table 2.26 for the hexagonal ammonium and potassium plutoryl (V) carbonates and have identified the compounds as $NH_4PuO_2CO_3$ and $KPuO_2CO_3$, respectively. The plutonium is bonded to two oxygens to form the collinear ion $[O\text{-}Pu\text{-}O]^+$, and also forms secondary bonds to carbonate oxygens, resulting in endless layers of average composition

Table 2.26 - X-RAY CRYSTALLOGRAPHIC DATA FOR ALKALI PLUTONYL (V) CARBONATES[101]

Compound	Symmetry	Space Group	Lattice Parameters, A a_o	c_o	Formula Units per Unit Cell
$NH_4PuO_2CO_3$	Hexagonal	$C6/mmc(D_{6h}^4)$	5.09±0.01	10.39±0.02	2
$KpuO_2CO_3$	Hexagonal	$C6/mmc(D_{6h}^4)$	5.09±0.01	9.83±0.02	2

$PuO_2CO_3^-$, which in turn are held together by the alkali metal ions located between layers.

The plutonyl (V) carbonates are stable only when in contact with carbonate solution, and are altered by washing with water.[100]

2-6.1.3 Plutonyl (VI) Carbonates. The intense green ammonium plutonyl (VI) carbonate, $(NH_4)_4PuO_2(CO_3)_3$, has been precipitated by Drabkina[102] by the reaction of dry ammonium carbonate with a weakly acid solution of plutonyl (VI). The product was washed with 15 percent ammonium carbonate and alcohol. It was found to be soluble in mineral acids, and its solubility in ammonium carbonate and nitrate solutions varies with their concentration, as shown in Table 2.27.

Upon storage in air several days or heating to 120 - 130°, the double carbonate decomposed to red PuO_2CO_3 according to the equation:

$$(NH_4)_4PuO_2(CO_3)_3 \rightarrow PuO_2CO_3 + 4NH_3 + 2CO_2 + 2H_2O$$

The monocarbonate in turn was found to decompose to PuO_2 if heated to 130 - 140°:

$$PuO_2CO_3 \rightarrow PuO_2 + CO_2 + 1/2O_2$$

The analogous potassium compound, $K_4PuO_2(CO_3)_3$, also green, has been precipitated by oxidation of plutonium to the hexavalent state in concentrated potassium carbonate solution at 95 - 100°, and dried to constant weight at 40 - 50°.[104]

2-6.2 Plutonium Oxalates. Stable oxalates of plutonium (III), (IV), and plutonyl (VI) are known, and due to their process importance, they have received considerable study. The present discussion is limited to their basic chemistry, while their use in the preparation of plutonium metal is described in Sec. IV, Chap. 2, Sec. 2-1.3 and 2-1.4.

2-6.2.1 Plutonium (III) Oxalate. Hydrated plutonium (III) oxalate may be precipitated from a dilute nitric acid solution of trivalent plutonium (prepared by reduction of the tetravalent ion with iodide) by the addition of

Table 2.27 - SOLUBILITY OF AMMONIUM PLUTONYL (VI) CARBONATE IN AMMONIUM CARBONATE AND NITRATE SOLUTIONS AT 20°[103]

$(NH_4)_2CO_3$ Conc., Wt. %	$(NH_4)_4PuO_2 \cdot (CO_3)_3$ Solubility, g/kg sol'n	NH_4NO_3 Conc. Wt.%	$(NH_4)_4PuO_2(CO_3)_3$ Solubility, g/kg sol'n	Wt.% NH_4NO_3 in Saturated $(NH_4)_2CO_3$ sol'n	$(NH_4)_4PuO_2(CO_3)_3$ Solubility, g/kg sol'n
5	3.53	10	2.32	5	0.28
10	1.90	20	0.83	10	0.21
15	0.97	30	0.42	15	0.16
20	0.66	40	0.17	20	0.13
25	0.40	50	0.077	25	0.10
		63.9 Saturated	0.021 0.027		

oxalic acid or sodium oxalate.[43,105] The product may be washed with water and alcohol and dried under vacuum at room temperature. Solubility data for plutonium (III) oxalate are reproduced in Tables 2.28 and 2.29.

There is a lack of general agreement on the degree of hydration of the precipitated oxalate. Thus Cunningham[108] states that the compound contains nine molecules of water of hydration, while Dawson and Elliott[43] obtained thermogravimetric evidence for ten. Similarly, there is disagreement on the temperatures required for dehydration and decomposition of the oxalate. In their thermogravimetric investigations, Dawson and Elliott found that the hydrated oxalate, in air at 180° or in vacuum at 230°, formed the dihydrate, $Pu_2(C_2O_4)_3 \cdot 2H_2O$, which then decomposed to the anhydrous oxalate at 200° in air or 350° in vacuum, (see Fig. III.5). Bakes et al.[109] found that the anhydrous compound could be prepared by heating the hydrate in air at 225° or in hydrogen below 300°. Decomposition of the oxalate to plutonium dioxide was reported to be appreciable at 300°, and almost complete at 400°.[108] The differential thermal analysis data of Kartushova and co-workers[110] tend to agree more with the latter results. Hydrated plutonium (III) oxalate was observed to be dehydrated completely by heating in air to 140°. In the 300 - 330° range, without access to air, a dark brown product was formed, which on the basis of chemical analysis was suggested to be $Pu(C_2O_4)(CO_3)_{0.5}$. At about 270° in the presence of air, or 460° without access to air, the oxalate was decomposed to plutonium dioxide. The reactivity of oxide prepared in this manner is greater than that made from other compounds,[108] with the result that the oxalate is the preferred starting compound for the preparation of plutonium dioxide.

2-6.2.2 Plutonium (IV) Oxalates. Yellow-green plutonium (IV) oxalate, $Pu(C_2O_4)_2 \cdot 6H_2O$, may be precipitated by the addition of oxalic acid to an

Table 2.28 - SOLUBILITY OF HYDRATED PLUTONIUM (III) OXALATE[106]

H^+ Conc., M	$H_2C_2O_4$ Conc., M	Pu Conc. in Supernate mg/liter
3.7	0.5	460
1.96	.2	290
0.75	.2	21
.22	.14	6

Table 2.29 - RATE OF PRECIPITATION OF PLUTONIUM (III) OXALATE FROM 0.75 MOLAR NITRIC ACID-0.25 MOLAR OXALIC ACID[107]

Time After Initial Mixing, Min.	Pu Conc. in Supernate, mg/liter
5	40.6
15	18.4
60	23.5
420	38.8

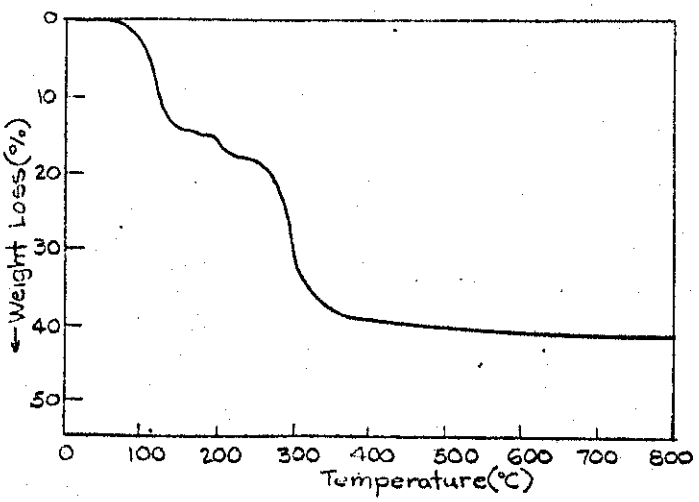

Fig. III.5 - Thermogravimetric curve for hydrated plutonium (III) oxalate in air.[43]

acidic solution of plutonium (IV).[9,43] It may be dried by washing with alcohol and holding under vacuum.

As can be seen in Table 2.30, the rate of precipitation of plutonium (IV) oxalate is slower than most precipitations, and constitutes one of the disadvantages of the oxalate process for metal preparation.

Kemp and Welch[111] found that the plutonium concentration in the supernate decreased during the first 100 - 500 hours, and then increased, presumably due to decomposition of the oxalate by nitric acid.

Careful determinations have been made of the solubility of plutonium (IV) oxalate in various solutions. The data of Mandleberg et al.,[45] given in Table 2.31, were obtained after agitating the oxalate in the respective solutions for periods of two to three weeks, in order to obtain optimum values.

Moskvin and Gel'man[112] found that aqueous solutions of plutonium (IV) oxalate displayed acidic properties. They also determined the solubility of this compound in various acids, and these results are shown in Table 2.32.

These results, where comparable, are higher than those of Table 2.31, principally because they were not equilibrated long enough for minimum solubility to be attained. It would thus appear that the data of Table 2.32 should be accepted with reservations. Nevertheless, they have been used to calculate a value for the solubility product of plutonium (IV) oxalate of 4×10^{-22}.[112]

Thermogravimetric curves for the decomposition of hydrated plutonium (IV) oxalate as a function of temperature and as a function of time at constant temperature are reproduced in Figs. III.6 and III.7, respectively. The former curve indicates that the precipitated oxalate has six molecules of water of hydration, and that it does not form stable carbonates or lower

Table 2.30 - RATE OF PRECIPITATION OF PLUTONIUM (IV) OXALATE FROM ONE MOLAR NITRIC ACID-0.1 MOLAR OXALIC ACID[113]

Time After Initial Mixing, hr.	Pu Conc. in Supernate, g/liter
0	0.22
0.5	.070
1	.036
2	.031
4	.028
7	.027
78	.025

Table 2.31 - SOLUBILITY OF PLUTONIUM (IV) OXALATE IN NITRIC ACID-OXALIC ACID SOLUTIONS AFTER 2 - 3 WEEKS' AGITATION AT 27°45

HNO_3 Conc., M	$H_2C_2O_4$ Conc., M	Solubility, mg Pu/liter
0	0	45.9
0	0.05	334
0	0.25	242
0.1	0	26.6
.1	0.5	132
.5	0	69.0
.5	0.05	26.6
.5	0.25	97.1
.5	0.60	361
.78	0.40	144
1.00	0	122
1.00	0.05	13.3
1.00	0.25	36.9
1.00	0.60	133
1.18	0.0071	16.3
1.61	0.002	65.8
1.61	0.015	15
2.00	0	128
2.00	0.05	9.7
2.00	0.25	15.1
2.34	0.01	15.3
2.34	0.005	24.9
2.52	0.025	16.7
3.52	0.005	92.1
3.52	0.01	45.8
3.52	0.05	18
3.52	0.1	18.2
3.52	0.5	21.4

Table 2.32 - SOLUBILITY OF PLUTONIUM (IV) OXALATE IN VARIOUS ACIDS AT 20°[112]

H_2SO_4 Conc., M	Solubility, g Pu/liter	HNO_3 Conc., M	Solubility, g Pu/liter	$HClO_4$ Conc., M	Solubility, g Pu/liter
0.025	0.031	0.025	0.11	0.1	0.13
0.1	0.045	0.1	0.14	0.5	0.24
0.5	0.12	0.25	0.25	1.0	0.38
1.0	0.19	0.5	0.33		
		1.0	0.66		

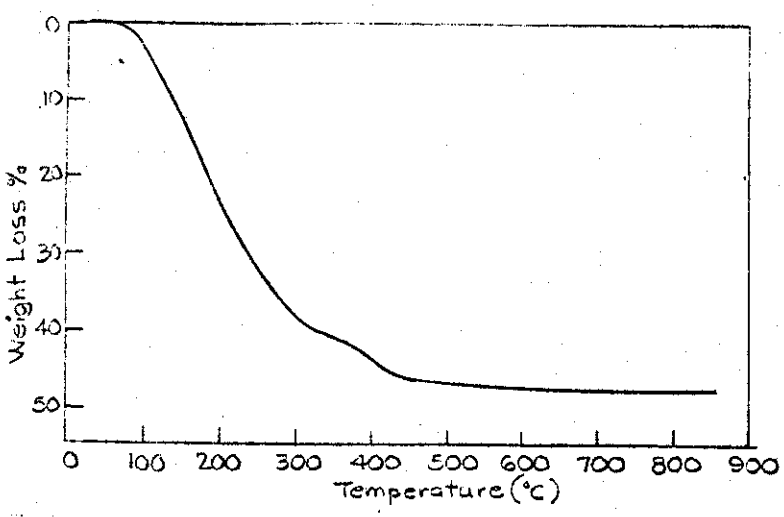

Fig. III.6 - Thermal decomposition of $Pu(C_2O_4)_2 \cdot 6H_2O$ in air.[43]

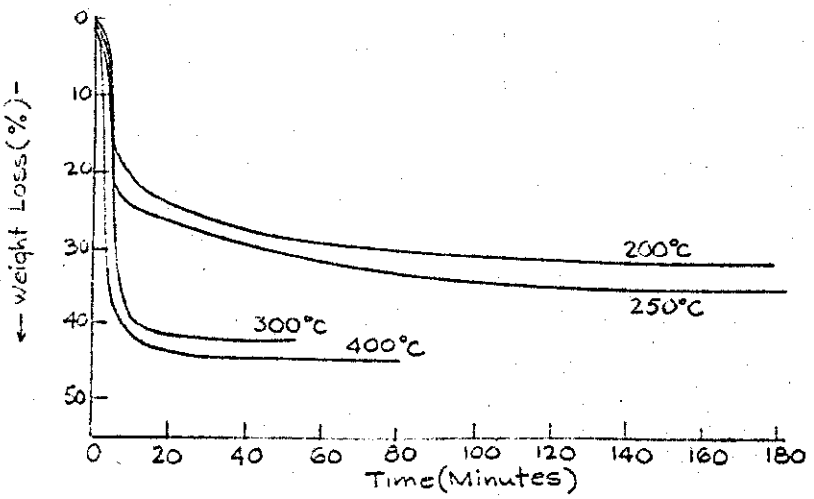

Fig. III.7 - Isotherms for $Pu(C_2O_4)_2.6H_2O$ in air.[43]

AEC-GE RICHLAND, WASH.

hydrated oxalates upon heating, but decomposes directly to the dioxide. Waterbury et al.[9], whose thermogravimetric curve is in general agreement with that in Fig. III.6, found that plutonium (IV) oxalate samples dried for different periods of time at 90° had from 1.47 to 4.64 molecules of water of hydration; all were hygroscopic at room temperature.

The isothermal curves of Fig. III.7 reveal that the oxalate can be heated to a constant weight even at temperatures below that necessary for attainment of the dioxide. The weight change for the 200° isotherm approximates that expected for formation of carbonate, but this is thought to be a coincidence, since the product did not evolve gas when treated with acid. The nature of the intermediates is not known. No X-ray pattern for the dioxide was obtained below about 400°, and the authors suggest that stoichiometric PuO_2 is not formed below about 600°. Actually, much higher temperatures are necessary. Waterbury and co-workers[9] found that heating to temperatures greater than 1250° was necessary for formation of the stoichiometric dioxide; heating to lower temperatures yielded a product with a slight excess of oxygen.

Kartushova et al.[110] studied the pyrolysis of the oxalate with limited access of air by differential thermal analysis, and collected the evolved gases for chemical analysis. They found that freshly precipitated (and dried) oxalate, when heated to 110°, evolved three molecules of water to form $Pu(C_2O_4)_2 \cdot 3H_2O$, while oxalates precipitated two or three hours before analysis evolved little, if any, gas. Heating to 170 - 200° caused the color to change to bright blue, and analysis of the evolved gases and solid residue indicated a reduction had taken place, with the formation of the trivalent plutonium oxalate, $Pu_2(C_2O_4)_3 \cdot H_2O$. At 380°, this compound was converted to plutonium dioxide. The contradictions between these results and those of Dawson and Elliott[43] are probably due to differences in storage time between precipitation and analysis and to the greater access of air in the latter authors' experiments.

Gel'man and Sokhina[114] have prepared several solid compounds containing plutonium (IV)-oxalate complex anion in 80 percent ethyl alcohol solution. Thus the addition of solid ammonium oxalate to a plutonium (IV) solution at 70 - 80° produced a red, syrupy liquid, which was air-dryed to a vitreous material that was shown by analysis to be $(NH_4)_6Pu(C_2O_4)_5 \cdot nH_2O$. This compound was isotropic and had a refractive index of 1.567.

Addition of sodium oxalate to a plutonium (IV) solution in alchohol again produced a red liquid, which, upon standing for 20 - 30 minutes, was transformed into a yellow-green solid. Analysis of the red material was not possible, but the yellow-green solid was found to be $Na_4Pu(C_2O_4)_4 \cdot 5H_2O$. In order to obtain larger crystals, the yellow-green compound was dissolved in water and the solution allowed to evaporate. Both the red and the yellow-green crystals separated simultaneously. The refractive indices for the former were found to be 1.55 and 1.52, while the latter had indices of 1.58 and 1.54. The red crystals were unstable, gradually reverting to the green form.

The potassium salt, $K_4Pu(C_2O_4)_4 \cdot 4H_2O$, was prepared in an analogous manner, and it also formed a red precipitate which gradually turned yellow. In this case, however, it was possible to analyze both the red and the yellow precipitates, and they were found to be identical chemically. Addition of excess potassium oxalate to a plutonium (IV) solution precipitated the compound $K_6Pu(C_2O_4)_5 \cdot 4H_2O$.

The complex oxalates were soluble in water and were shown by conductance studies to ionize into alkali ions and a complex plutonium oxalate anion. The compounds of the type $M_4Pu(C_2O_4)_4$ formed solutions with pH 4.5 - 4.7, while the $M_6Pu(C_2O_4)_5$ compounds yielded solutions whose pH was in the range 5.5 - 5.9. Increasing the pH to 7.5 - 8 caused decomposition of the complex anion with the precipitation of plutonium hydroxide. Likewise, the complex anion was destroyed by acidification.

Over a period of time, the complex alkali metal oxalate compounds were decomposed by alpha radiation, first to $Pu_2(C_2O_4)_3 \cdot nH_2O$, and ultimately to a mixture of $PuOCO_3$ and sodium or potassium carbonate.

2-6.2.3 Plutonyl (VI) Oxalate. Plutonyl (VI) oxalate, $PuO_2C_2O_4 \cdot 3H_2O$, was separated as a red precipitate by the addition of crystalline oxalic acid to a 1.5 - 2 normal nitric acid solution of plutonyl (VI) (prepared by oxidation with potassium dichromate or manganese dioxide).[115] The dried precipitate was found to change color gradually from red to green due to reduction of the plutonium by alpha emission. Upon heating to 180°, the plutonyl (VI) oxalate was observed to decompose explosively.

The oxalate was found to be only slightly soluble in water and dilute mineral acids, but soluble in dilute aqueous solutions of ammonium carbonate and ammonium oxalate.

The solubility of the oxalate in nitric acid-oxalic acid and nitric acid-ammonium oxalate mixtures at 20° has been measured by determining the plutonium content of the solution (by alpha-counting) after a two-hour agitation period. The results are given in Tables 2.33 and 2.34.

The greater solubility of plutonyl (VI) oxalate in nitric acid solutions containing ammonium oxalate than in those containing equivalent concentrations of oxalic acid was interpreted as evidence for the formation of oxalate complexes of plutonyl (VI) (see Sec. 3-3.4.5), although, as can be seen in Tables 2.33 and 2.34, the effect is not great. It was found that one mole of ammonium oxalate in solution could dissove one mole of plutonyl (VI) oxalate, leading to the conclusion that the simplest complex formed upon dissolution is $(NH_4)_2PuO_2(C_2O_4)_2$.

Table 2.33 - SOLUBILITY OF PLUTONYL (VI) OXALATE IN NITRIC ACID-OXALIC ACID SOLUTIONS AT 20°[115]

HNO_3 Conc., M	Solubility, g Pu/liter in Presence of Various $H_2C_2O_4 \cdot 2H_2O$ Concs. in Wt. %					
	0	1	2	4	6	8
1.1	3.2	0.95	0.64	0.59	0.51	0.49
2.0	3.91	1.28	0.91	0.62	0.57	0.49
3.08	6.75	2.35	1.3	0.76	0.61	0.59

Table 2.34 - SOLUBILITY OF PLUTONYL (VI) OXALATE IN NITRIC ACID-AMMONIUM OXALATE SOLUTIONS AT 20°[115]

HNO_3 Conc., M	Solubility, g Pu/liter in Presence of Various $(NH_4)_2C_2O_4 \cdot H_2O$ Concs. in Wt. %				
	1	2	3	4	6
0.5	0.71	0.92	1.60	-	-
1.0	0.90	0.80	0.77	0.87	1.16
2.0	1.66	1.19	0.81	0.71	0.63
3.0	2.51	1.44	1.17	0.93	0.76

2-7 PLUTONIUM SULFATES

Sulfates of plutonium (III) and (IV) have been prepared and characterized, and will be discussed individually below. At present no hexavalent plutonium sulfate is known.

2-7.1 Plutonium (III) Sulfates. A hydrated sulfate of plutonium (III) has been prepared by adding an equal volume of ethyl alcohol to a plutonium solution that had been saturated with sulfur dioxide for 18 hours.[116] The plutonium (IV) initially present was reduced to the trivalent state by the sulfur dioxide (precipitate formed at this point was dissolved by heating to 90° for one hour); upon addition of the alcohol a white precipitate formed, which after several hours changed to violet crystals of plutonium (III) sulfate hydrate, probably the heptahydrate, $Pu_2(SO_4)_3 \cdot 7H_2O$. The light blue-gray anhydrous salt may be formed from the hydrate by drying at 130 - 150°, preferably in an inert atmosphere.

The solubility of the trivalent sulfate is approximately 125 grams (as plutonium) per liter in 0.1 molar sulfuric acid; the solubility is lower by a factor of approximately 100 in 75 percent ethyl alcohol solutions.[116]

Two sulfate double salts of plutonium (III) have been reported by Anderson;[117] both are blue. The sodium salt, $NaPu(SO_4)_2 \cdot 4H_2O$, was prepared by adding a plutonium (III) sulfate solution in two molar sulfuric acid, and half this volume of methyl alcohol, to the appropriate volume of 0.5 molar sodium sulfate solution. The thallous compound, $TlPu(SO_4)_2 \cdot 4H_2O$, resulted when methyl alcohol was added to a 0.6 molar sulfuric acid solution containing the appropriate concentrations of plutonium (IV) and thallium (I) sulfates. Approximately one hour was required for precipitation.

2-7.2 Plutonium (IV) Sulfates. Anhydrous $Pu(SO_4)_2$ may be prepared by evaporating plutonium (IV) solutions containing excess sulfuric acid and

heating carefully to 450 - 600° to remove the excess acid.[43,118] This method has been confirmed by thermogravimetric studies[9,43] which also indicated that the sulfate is stable in air up to 650°, at which point it rapidly decomposes to the dioxide.

The anhydrous sulfate is a pink, hygroscopic salt, soluble in water and 5 normal acids, although sometimes crystals of an insoluble hydrate will separate from the latter.[118] The stability of an aqueous plutonium sulfate solution depends on the concentration of the salt; more dilute solutions rapidly becoming turbid. Warren and Brunstad[119] have studied the solubility of plutonium (IV) sulfate in nitric acid at various concentrations and temperatures; their results, given in Table 2.35, indicate that the solubility decreases with increasing nitric acid concentration.

Anderson[120] has prepared and identified three complex sulfates of plutonium (IV); all are green in color. The potassium salt, $K_4Pu(SO_4)_4 \cdot \sim 1H_2O$, was made by mixing dilute sulfuric acid solutions of potassium and plutonium (IV) sulfates and adding methyl alcohol. Initially $Pu(SO_4)_2$ precipitated, but this changed to the double salt on standing in the supernatant solution. The The ammonium salt, $(NH_4)_4Pu(SO_4)_4 \cdot \sim 2H_2O$, was prepared by mixing solutions of the appropriate sulfates, adding approximately an equal volume of methyl alcohol, and allowing to stand overnight. Rubidium plutonium sulfate, $Rb_4Pu(SO_4)_4 \cdot \sim 2H_2O$ resulted when plutonium (IV) sulfate was dissolved in 0.2 molar sulfuric acid - 20 percent ethyl alcohol containing rubidium sulfate. The exact degree of hydration of each of these salts is not known.

By saturating a one-normal sulfuric acid solution of plutonium sulfate with the appropriate alkali sulfate, Lipis and co-workers[121] have prepared the following compounds: yellow-rose $Na_6Pu(SO_4)_5 \cdot H_2O$, red $(NH_4)_6Pu(SO_4)_5 \cdot 2 - 4H_2O$, green $K_4Pu(SO_4)_4 \cdot 2H_2O$, rose-violet $Rb_4Pu(SO_4)_4$, and pale rose

Table 2.35 - CONCENTRATION OF PLUTONIUM (IV) IN EQUILIBRIUM WITH VARIOUS SULFATE CONCENTRATIONS IN NITRIC ACID[119]

2 M HNO_3, 25°C		4 M HNO_3, 25°C		6 M HNO_3, 25°C		6 M HNO_3, 55°C	
Plutonium g/liter	$SO_4^=$, M	Plutonium g/liter	$SO_4^=$, M	Plutonium g/liter	$SO_4^=$, M	Plutonium g/liter	$SO_4^=$, M
234	0.183	249	0.126	218	0.063	249	0.110
168	0.203	61.2	0.122	176	0.103	118	0.117
135	0.198	18.1	0.360	136	0.093	39.8	0.146
113	0.188	12.6	0.469	107	0.098	14.3	0.270
73.4	0.182	7.5	0.738	71.9	0.094	3.45	1.19
61.2	0.258			52.6	0.124	2.22	1.57
57.4	0.390			50.7	0.102	1.71	1.80
53.5	0.314			32.0	0.171	1.39	2.11
47.0	0.232			17.0	0.234		
39.9	0.315			16.7	0.232		
38.5	0.424			2.46	1.06		
38.5	0.452			1.38	1.48		
35.8	0.249						
35.4	0.323						

$Cs_4Pu(SO_4)_4$. A lithium salt of undetermined composition was also prepared. The fact that the rubidium salt differs in color from the salt prepared by Anderson is apparently due to the absence of water of hydration; both the rubidium and cesium salts turned green upon standing in the air for an extended period. The compounds are readily dissolved in water and mineral acids, and hydrolyze in aqueous solution. Their absorption spectra differ greatly from one another, and from that of plutonium (IV) sulfate.

2-8 PLUTONIUM NITRATES

Plutonium (IV) nitrate pentahydrate, $Pu(NO_3)_4 \cdot 5H_2O$, has been prepared by allowing a concentrated solution of plutonium (IV) in nitric acid to evaporate at room temperature for a period of several months.[122] As soon as crystal nuclei appear (or have been added) the rate of crystallization may be increased by evaporating in a current of air. The product crystals are green if smaller than about one millimeter; larger crystals appear to be black. They are fairly stable, both in humid and dry air.

A thermogravimetric study of the hydrate revealed that it began to decompose at 40°, and to melt, or deliquesce at 95 - 100°.[122] After rapid decomposition around 100°, a fairly unstable intermediate product was formed between 150 and 220°. (This intermediate compound dissolved in water or nitric acid to yield plutonyl (VI) nitrate, $PuO_2(NO_3)_2$, and is believed to be a basic plutonyl nitrate.) Decomposition above 220° was very rapid; at 250° conversion to the dioxide was essentially complete, although there continued to be a slight weight loss above this temperature. The ignition of the nitrate at 1250° produces oxygen-deficient plutonium dioxide.[9]

Plutonium nitrate pentahydrate is readily soluble in water, the stability of the solution being dependent on the concentration of the salt. Thus a dilute solution, which is brown initially, soon changes to green as colloidal plutonium forms. Since the colloid does not form in solutions of high nitrate ion concentration, the concentrated solutions of the salt remain brown. Solutions of the nitrate in concentrated nitric acid are green, due to a plutonium-nitrate complex (see Sec. 3, Chap. 3). Acetone and ether solutions of the nitrate are also green.

Dawson[124] has determined the solubility of plutonium (IV) nitrate in dibutylcarbitol ("butex") containing various concentrations of nitric acid.

At 25° the solubility varied from 0.71 grams of plutonium per liter in butex 0.1 normal in nitric acid to 5.6 grams of plutonium per liter when the nitric acid concentration in the solvent was 1.5 normal. Solubilities were somewhat higher at 35°.

Staritzky[123] has made an X-ray diffraction study of $Pu(NO_3)_4 \cdot 5H_2O$, from which he determined the crystallographic data reproduced in Table 2.36.

Several complex salts of plutonium (IV) nitrate are known. An ammonium double salt, $(NH_4)_2Pu(NO_3)_6 \cdot 2H_2O$, has been obtained by evaporating a one-molar nitric acid solution containing equimolar concentrations of plutonium (IV) and ammonium nitrate.[125] Crystals of pale green potassium plutonium hexanitrate, $K_2Pu(NO_3)_6$, were formed by cooling to 1° a 12 molar nitric acid solution containing the appropriate concentrations of potassium and plutonium (IV) nitrates.[126] The pale green rubidium and cesium double salts, $Rb_2Pu(NO_3)_6$ and $Cs_2Pu(NO_3)_6$, are formed when nitric acid solutions of the respective nitrates are mixed with plutonium (IV) nitrate solutions. Pyridinium and quinolinium double salts, $(C_5H_5NH)_2Pu(NO_3)_6 \cdot \sim 14H_2O$ and $(C_9H_7NH)_2Pu(NO_3)_6$, were made by mixing the appropriate nitrate solutions. The solubilities of the latter four salts were low enough that crystallization could be effected without cooling the solutions. Plutonium (IV) tetraethyl ammonium nitrate, $[(C_2H_5)_4N]_2Pu(NO_3)_6$ has been prepared as a needle-like precipitate by Ryan[127] by the gradual mixing of solutions of plutonium (IV) nitrate and tetraethylammonium nitrate in stoichiometric amounts. The solutions were added alternately in small portions to avoid large excesses of either reactant. The precipitate was digested at 25° for 24 hours before filtering. A tetrabutylammonium salt was prepared in an analogous manner and assumed to be $[(C_4H_9)_4N]_2Pu(NO_3)_6$.

Table 2.36 - X-RAY CRYSTALLOGRAPHIC DATA OF PLUTONIUM NITRATE PENTAHYDRATE[123]

Symmetry:	Orthorhombic
Space Group:	$Fdd2(C_{2v}^{19})$
Lattice Constants:	$a_o = 11.14 \pm 0.02$ A
	$b_o = 22.58 \pm 0.03$ A
	$c_o = 10.51 \pm 0.03$ A
Formula Units per Unit Cell:	8
Calculated Density:	2.90 g/cm^3
Refractive Indices (5893A):	1.554_5, 1.556, 1.667

Ryan[128] has prepared a plutonyl (VI) nitrate salt, $(C_2H_5)_4NPuO_2(NO_3)_3$, by the addition of a nitric acid solution of tetraethylammonium nitrate to a solution of plutonyl (VI) (prepared by ozone oxidation) in eight molar nitric acid and cooling to produce needle-like crystals that melted around 100°. The compound was unstable, possibly due to alpha-decomposition.

2-9 PLUTONIUM PHOSPHATES

Phosphate chemistry has been of continuing importance in plutonium separations technology. Early processes were based on bismuth phosphate carrier precipitation; now this process has been abandoned in favor of solvent extraction, of which the tributyl phosphate process is the most important. It is not surprising therefore that plutonium phosphates have been and still are the objects of considerable study. X-ray crystallographic data for some of the phosphates are given in Table 2.37.[129]

2-9.1 Plutonium (III) Phosphate. Plutonium (III) phosphate hemihydrate $PuPO_4 \cdot 0.5H_2O$, was prepared originally by adding phosphoric acid (to 0.8 molar) to a solution of plutonium in 0.5 molar sulfuric acid saturated with sulfur dioxide, sealing, and heating at 75° for 2.5 hours.[130] Another method is that of Bjorklund[129], who added 200 milliliters of 0.4 molar $PuCl_3$ solution in one normal hydrochloric acid, and 400 milliliters of 0.5 molar $(NH_4)_2HPO_4$ solution at rates of five and nine milliliters per minute, respectively, to 400 milliliters of 0.07 molar hydrochloric acid to 80 - 90°. The pale blue precipitate was digested for one hour at 80 - 90° with stirring and 64 hours at 25 - 30° without stirring, after which it was filtered, washed, and dried at 100 - 150°.

Anhydrous plutonium (III) phosphate may be prepared by two methods:[129]

1. The hemihydrate, $PuPO_4 \cdot 0.5H_2O$, may be dried to constant weight at 950° in air to form $PuPO_4$.

2. Bjorklund[129] prepared a pink plutonium oxalatophosphate by the simultaneous addition of a phosphoric acid solution of plutonium (IV), (prepared by the dissolution of plutonium (IV) peroxide) and a 0.55 molar aqueous solution of oxalic acid to 85 percent phosphoric acid stirred at 100°. The final reactant concentrations were in the ratio $[Pu]/[H_2C_2O_4]/[H_3PO_4] = 1/10/37$. The temperature was kept at 80 - 100° during the five hours of reagent addition and during

the 16-hour digestion period. The solution was then held at 25 - 30° for 24 hours while stirring continued. The precipitate was filtered, washed with 0.1 molar oxalic-0.1 molar phosphoric acid solution, water, and absolute ethyl alcohol, and dried in a stream of air at room temperature. The product thus obtained had a $Pu/C_2O_4/PO_4$ ratio of 1.00/1.58/1.03 and has been called an "oxalatophosphate", although it is not necessarily a discrete chemical compound. The product was decomposed to anhydrous $PuPO_4$ by heating slowly to 950° in air and holding at that temperature until constant weight was reached.

Qualitative solubility data for plutonium phosphate in various acids has been determined by Bjorklund,[129] and is reproduced in Table 2.38.

Plutonium (III) phosphate is stable in air at 1000°, but decomposes, without melting, to PuO_2 when held at 1400 - 1500° under 10^{-4} mm pressure.[129]

2-9.2 Plutonium (IV) Phosphates. Plutonium (IV) hydrogen phosphate, $Pu(HPO_4)_2 \cdot xH_2O$, may be prepared as a white gelatinous precipitate by the addition of phosphoric acid to an acidic plutonium solution.[131] It should be washed with 1 - 2 normal nitric or hydrochloric acid; washing with more dilute acid apparently causes partial conversion to $Pu_2H(PO_4)_3 \cdot yH_2O$.

Denotkina and co-workers[132,133] have studied the solubility of $Pu(HPO_4)_2 \cdot xH_2O$ in various acids; their results are reproduced in Table 2.39. From the data they determined the solubility product, $K_{S.P.}$, of $Pu(HPO_4)_2 \cdot xH_2O$ to be 2×10^{-28}.[132]

Red plutonium hydrogen triphosphate, $Pu_2H(PO_4)_3 \cdot xH_2O$, has been made by heating $Pu(HPO_4)_2 \cdot xH_2O$ (see above) in a 1.45 molar nitric-1.0 molar phosphoric acid mixture at 110° for several days.[131] Attempts to dissolve it in acid solution apparently converted it back to the hydrogen phosphate.

When $Pu(HPO_4)_2$ is heated in 1.8 molar nitric-0.4 molar phosphoric acid in a sealed tube at 110° for several days, plutonium tetraphosphate,

Table 2.37 - X-RAY AND OPTICAL CRYSTALLOGRAPHIC DATA FOR PLUTONIUM PHOSPHATES[129]

Compound	Color	Symmetry	Lattice Constants, A a_o	b_o	c_o	Refractive Index	Calculated Density, g/cm^3
$PuPO_4 \cdot 0.5H_2O$	Blue	Hexagonal	7.011±0.002	-	6.401±0.002	1.76	6.27
$PuPO_4$	Blue	Monoclinic	6.73±0.02	7.00±0.02 $\beta = 103.8° \pm 0.4°$	6.42±0.02	1.85_5, 1.86, 1.90_5	7.55
PuP_2O_7	Colorless	Cubic	8.560±0.006	-	-	1.67_6	4.37

Table 2.38 - SOLUBILITY* OF PLUTONIUM (III) PHOSPHATE IN VARIOUS SOLUTIONS[129]

Solution	Temperature	
	25 - 30°	90 - 100°
Concentrated HCl	Slight	Complete
Concentrated HNO_3	Incomplete	Complete
Concentrated H_2SO_4	-	Complete**
85 percent H_3PO_4	Negligible	Incomplete
Glacial acetic acid	-	No reaction
6 normal NaOH	-	Incomplete***

* 1 gram sample stirred 4 - 5 hours with 25 milliliters of each solution.

** Metathesis occurred; product insoluble in concentrated acid but soluble in dilute acid.

*** Metathesis occurred; product insoluble in NaOH or water, but soluble in acid.

$Pu_3(PO_4)_4 \cdot xH_2O$, was formed.[131] Note that this preparation is similar to that for the triphosphate, with the exception of the acid concentrations used.

Anhydrous plutonium (IV) pyrophosphate, PuP_2O_7, has been prepared by Bjorklund[129] by the thermal decomposition of plutonium oxalatophosphate intermediates. As described in the preparation of plutonium (III) phosphate (see above), these intermediates are not necessarily discrete stoichiometric compounds. Whereas the oxalatophosphate with a P/Pu ratio of one decomposes to $PuPO_4$, an oxalatophosphate with a P/Pu ratio of two is necessary to yield the pyrophosphate. Two preparative schemes have been described by Bjorklund:[129]

1. A plutonium (IV) phosphate solution (made from the peroxide) was added slowly to a 0.9 molar solution of oxalic acid in 85 percent phosphoric acid at 90 - 100°. The final reactant concentrations were in the ratio $[Pu]/[H_2C_2O_4]/[H_3PO_4] = 1/5/100$. The pink precipitate formed was digested with stirring at this temperature for 2.5 hours and then at room temperature without stirring for 65 hours. It was filtered, washed with 0.1 molar oxalic-0.1 molar phosphoric acid, water, and absolute ethyl alcohol, and dried in a stream of air at room temperature. This material was decomposed to PuP_2O_7 by slowly heating in air to 950° and holding there until constant weight was attained.

2. Addition of a 95 percent phosphoric acid solution of plutonium (IV) (dissolved oxalate) to a five molar aqueous oxalic acid solution at 70 - 100° precipitated the pink oxalatophosphate. (Reactant ratios: $[Pu]/[H_2C_2O_4]/[H_3PO_4] = 1/10/20$.) The precipitate was digested five hours at this temperature, then digested at room temperature, filtered, washed, dried, and ignited to PuP_2O_7 exactly as described in Procedure 1.

If the P/Pu ratio of the oxalatophosphate intermediate is less than 2/1, it may be raised to this value by the admixture of $NH_4H_2PO_4$ before ignition.

Table 2.39 - SOLUBILITY OF PLUTONIUM (IV) HYDROGEN PHOSPHATE IN VARIOUS SOLUTIONS AT 25°[132,133]

Distilled water = 3.5×10^{-6} moles/liter

H_3PO_4 in 2 N HNO_3		HNO_3 - $LiNO_3$ Solutions			$HClO_4$ - $NaClO_4$ Solutions		
H_3PO_4 Conc., M	Solubility, M/liter x 10^4	HNO_3 Conc., M	$LiNO_3$ Conc., M	Solubility, M/liter x 10^4	$HClO_4$ Conc., M	$NaClO_4$, Conc., M	Solubility, M/liter x 10^4
0.012	8.5				0	2.0	0.0059
0.02	4.58	0	2.0	0.798	0.1	1.9	0.99
0.028	3.0	0.1	1.9	0.257	0.3	1.7	0.66
0.04	1.96	0.3	1.7	1.95	0.6	1.4	1.55
0.06	0.13	0.6	1.4	2.40	1.0	1.0	3.73
0.071	1.11	1.0	1.0	6.47	1.4	0.6	5.47
0.101	1.06	1.41	0.59	17.6	2.0	0	7.17
0.20	1.33	1.7	0.3	21.3			
0.25	1.44	2.0	0	27.5			
0.40	1.88						
0.63	3.31						
0.80	4.1						
1.20	7.74						
1.60	13.6						
2.00	29.0						

Ratios of P/Pu between 1/1 and 2/1 will result in a mixture of $PuPO_4$ and PuP_2O_7.[129]

Qualitative solubility data for plutonium (IV) pyrophosphate are given in Table 2.40.[129]

Comparison of this table with Table 2.38 indicates that $PuPO_4$ and PuP_2O_7 may be separated from one another at room temperature by the use of hydrochloric of phosphoric acid, which dissolve the latter. In synthesis, however, it is preferable to control the P/Pu ratio carefully so that an unmixed product is obtained, as explained above.

Although PuP_2O_7 can be heated to 1000° in air with no loss in weight, under 5×10^{-5} millimeters of pressure at this temperature it slowly converts to $PuPO_4$.[129] Decomposition is more rapid at 1200 - 1400°.

Moore[134] has precipitated white plutonium (IV) monobutyl phosphate, $Pu(C_4H_9PO_4)_2 \cdot xH_2O$, by the addition of monobutyl phosphate (MBP) to a plutonium (IV) solution in three molar nitric acid, and studied its solubility extensively. His results are given in Table 2.41.

The solubility was found to be affected only slightly, if at all, by the presence of dibutyl phosphate, or by increasing the temperature to 55°.

Table 2.40 - SOLUBILITY* OF PLUTONIUM (IV) PYROPHOSPHATE IN VARIOUS SOLUTIONS[129]

Solution	Temperature 25 - 30°	90 - 100°
Concentrated HCl	Complete	Complete
Concentrated HNO_3	Slight	Incomplete
Concentrated H_2SO_4	Complete**	Complete**
85 percent H_3PO_4	Complete	Complete
Glacial acetic acid	-	Negligible
6 normal NaOH	-	Complete***

* 1 gram sample stirred 4 - 5 hours with 25 milliliters of each solution.

** Metathesis occurred; product insoluble in concentrated acid, but soluble in dilute acid.

*** Metathesis occurred; product insoluble in NaOH or water, but soluble in acid.

Table 2.41 - SOLUBILITY OF PLUTONIUM (IV) MONOBUTYL PHOSPHATE AT 25° AS A FUNCTION OF NITRIC ACID AND MONOBUTYL PHOSPHATE CONCENTRATIONS[134]

Initial plutonium concentrations: 20 - 80 mg/liter			
Nitric Acid - 1 vol. % MBP		3 Molar Nitric Acid - Indicated MBP	
HNO_3 Conc., M	Solubility, mg plutonium	MBP Conc., M	Solubility, mg plutonium/liter
0.6	0.306	0.0006	>20
1.6	0.333	0.0031	>20
3.0	0.45	0.0062	13.2
5.0	0.664	0.0187	1.47
10	3.93	0.031	0.72
15	43.2	0.062	0.45
		0.075	0.34
		0.124	0.42
		0.230	0.41
		0.311	0.59
		0.622	1.21
		1.24	22.2

2-10 PLUTONIUM CARBIDES AND SILICIDES

Plutonium carbides are currently under development for use as high-temperature reactor fuels, and similar studies are planned for the silicides. The fabrication and reactor applications of these materials are discussed in Sec. II, Chap. 6; the present discussion will be limited to their preparation and chemical properties. X-ray crystallographic data for the carbides and silicides are given in Table 2.42.

2-10.1 Plutonium Carbides. Plutonium monocarbide has been prepared by Drummond and co-workers[135] by heating powdered graphite in an inert atmosphere with:

1. plutonium hydride at 800° for four hours,
2. plutonium metal at 1000° for five hours, or
3. plutonium dioxide at 1800° for ten minutes.

In each case a sintered coke-like material was obtained which could be broken into gray crystalline fragments. The product made from the hydride was the purest, but it contained small quantities of plutonium metal and graphite. Samples prepared from the dioxide contained no plutonium metal, but were contaminated with the sesquicarbide.

Plutonium monocarbide oxidizes slowly in air at 200 - 300°, and burns brightly at about 400°.[135] It melts in an inert atmosphere at about 1850°. Samples have shown no evidence of reaction after standing in air at room temperature for two months; PuC prepared from the hydride, being more porous, is the most reactive.

Plutonium monocarbide is much more reactive than its uranium analog. While not attacked by cold water, PuC reacts with hot water to form plutonium (III) hydroxide and a gas mixture consisting of hydrogen and methane as well as smaller amounts of ethan, ethylene, acetylene, butanes, and butenes.[135]

Table 2.42 - X-RAY CRYSTALLOGRAPHIC DATA FOR PLUTONIUM CARBIDES AND SILICIDES[5]

Compound	Symmetry	Space Group	Lattice Constants, A a_o	b_o	c_o	Formula Units per Unit Cell	Calculated Density gm/cm^3
PuC	Face-Centered Cubic	Fm3m	4.97±0.01	-	-	4	13.6
Pu_2C_3	Body-Centered Cubic	$I\bar{4}3d$	8.129±0.001	-	-	8	12.70
PuSi	Orthorhombic	Pbnm	5.727±0.005	7.933±0.003	3.847±0.001	4	10.15
Pu_2Si_3	Hexagonal	P6/mmm	3.876±0.002 c/a = 1.055	-	4.090±0.002		8.77
$PuSi_2$	Body-Centered Tetragonal	I4/amd	3.967±0.001	-	13.72±0.03	4	9.08

Cold nitric acid attacks PuC only slightly, but hot concentrated nitric acid containing a small amount of sodium fluoride reacts with the carbide, forming a deposit of carbon.

Plutonium sesquicarbide, Pu_2C_3, has been prepared by heating an intimate mixture of the stoichiometric quantities of the dioxide and graphite in an inert atmosphere at 1850° for ten minutes.[135] The product, which closely resembled the monocarbide it frequently contained as an impurity, melted at about 1900°.

Chemical properties of the sesquicarbide differ only slightly from those of the monocarbide. The sesquicarbide appears to be more stable toward oxidation at elevated temperatures, and toward hydrolysis by acids and boiling water. Its hydrolysis products include solid and liquid hydrocarbons, as well as a mixture of gaseous hydrocarbons similar to that formed by PuC. The sesquicarbide seems less stable toward atmospheric hydrolysis than the monocarbide.

Drummond et al.[135] found evidence of a higher carbide of plutonium. Several samples prepared at temperatures above 2000° in the presence of excess graphite gave X-ray diffraction patterns unlike those of either PuC or Pu_2C_3. This higher carbide, which melts at about 2200°, cannot be prepared at temperatures lower than about 2000°. It is much less stable toward atmospheric hydrolysis than the other carbides, but is more oxidation resistant.

The compound has not been identified, and therefore its existence cannot be regarded as definite until more proof is obtained.

2-10.2 Plutonium Silicides. Plutonium forms several compounds with silicon; PuSi, Pu_2Si_3, and $PuSi_2$ have been prepared and identified by X-ray diffraction, while Pu_5Si_3 and Pu_3Si_2 probably exist but have not been identified.[136] The disilicide has been prepared by heating a mixture of PuF_3 and $CaSi_2$ (mole ratio of 10/3) in vacuum to 1550°,[137] and has an estimated heat of

formation of -211 kcal/mole.[95] All the silicides of plutonium may be made by reacting the trifluoride with silicon in vacuo at elevated temperatures.[136] They are hard, brittle, and metallic in appearance, and are oxidized in air at 700° to PuO_2.[137]

2-11 PLUTONIUM NITRIDE, PHOSPHIDE, AND ARSENIDE

Plutonium nitride, PuN, may be prepared in good yield by reacting the hydride with:

1. ammonia vapor (250 mm pressure) at 650°,[138] or
2. nitrogen at temperatues of 240° or above.[139]

The reaction of nitrogen with plutonium metal begins at about 300° but is very slow: conversion to the nitride was only 78 percent complete even after 17 hours at 1000°.[139] It is brown to black, and hard, though somewhat brittle.

In contrast to the uranium nitrides, plutonium nitride is relatively reactive and easily decomposed.[139] Complete hydrolysis in moist air occurs within a few days at room temperature, or within a few hours at 80 - 90° to produce PuO_2.

Although PuN is hydrolyzed only slowly by cold water, it reacts rapidly with boiling water to form a bulky black mass. It can be dissolved in three molar hydrochloric or sulfuric acids, to yield a blue plutonium (III) solution, although a small amount of residue (presumably a hydrolysis product) remains. The sulfate solution gradually turns pink as the plutonium is air-oxidized to the tetravalent state. Plutonium nitride reacts only slowly with nitric acid, even on heating, producing a plutonium nitrate solution and a black hydrated oxide. The relative proportions of the two products depend on concentration of acid, time of heating, and particle size of the nitride; in general, higher nitric acid concentrations favor dissolution to form the nitrate.

X-ray crystallographic data for PuN are reproduced in Table 2-43.

Plutonium phosphide and arsenide, PuP and PuAs, were prepared by direct combination of the respective elements.[142] Mixtures of phosphorus or arsenic with plutonium were inductively heated under vacuum or in helium at a pressure of slightly less than one atmosphere. In each case the reaction was strongly

exothermic; the resulting compounds, therefore, apparently are quite stable. They seem to decompose, without melting, in the vicinity of 2000°. Efforts to prepare compounds with P/Pu and As/Pu ratios other than 1/1 were unsuccessful.

Table 2.43 gives X-ray data for these compounds.

Table 2.43 - X-RAY CRYSTALLOGRAPHIC DATA FOR PLUTONIUM NITRIDE, PHOSPHIDE, AND ARSENIDE*

Compound	Symmetry	Space Group	Lattice Parameters, A a_o	Formula Units per Unit Cell	Calculated Density, g/cm^3
PuN	Face-Centered Cubic	-	4.905±0.002[139]	-	14.25[140]
PuP	Face-Centered Cubic	Fm3m	5.644±0.004	4	9.87
PuAs	Face-Centered Cubic	Fm3m	5.855±0.004	4	10.39

* Data from Coffinberry and Ellinger[5] except as otherwise noted.

2-12 PLUTONIUM SULFIDES, OXYSELENIDE AND TELLURIDE

Although the sulfides and tellurides of plutonium have received very little study, their X-ray crystallographic data have been determined, and are given in Table 2.44.

Plutonium sulfide, PuS, was apparently formed in an attempt to reduce PuF_3 with calcium vapor in a barium sulfide crucible at 1250°.[143] The compound, which had a bronze, metallic appearance, has been partially identified chemically and its existence is probable, although not certain.

Plutonium trisulfide-tetrasulfide, Pu_2S_3-Pu_3S_4, was prepared by heating $PuCl_3$ in a stream of purified hydrogen sulfide gas for one hour at 840° and for another hour at 916°.[143] It was also made by heating plutonium (IV) hydroxide in a stream of hydrogen sulfide to 1340° and holding there for two hours. The sulfide prepared from the hydroxide was shown to be isomorphous with Ce_2S_3-Ce_3S_4; that from $PuCl_3$ was not isomorphous with Ce_2S_3-Ce_3S_4, and was found to be Pu_2S_3.[143] Thus the stoichiometry and crystal habit of the product sulfide appears to be greatly influenced by its preparative history. Both products were black, but that from $PuCl_3$ had a deep purple tinge.

A plutonium oxysulfide, Pu_2O_2S, was made in 70 percent yield by passing dry, purified hydrogen sulfide over $Pu(OH)_4$, heating over a one-hour period to 1225 - 1300°, and holding at this temperature for 45 minutes.[144] The product obtained was hard and had a metallic luster.

Plutonium telluride, PuTe, has been prepared by Gorum[142] by inductively heating a 1/1 mixture of plutonium and tellurium in vacuo or under slightly less than one atmosphere pressure of helium. The reaction is very exothermic, indicating formation of a stable compound; the product appears stable up to about 2000°, at which point it decomposes without melting.

Table 2.44 - X-RAY CRYSTALLOGRAPHIC DATA FOR PLUTONIUM SULFIDES, OXYSELENIDE, AND TELLURIDE*

Compound	Symmetry	Space Group	Lattice Parameters, A a_o	Lattice Parameters, A c_o	Formula Units per Unit Cell	Calculated Density, g/cm^3
PuS	Face-Centered Cubic		5.536±0.001	-	-	10.60
Pu_2S_3 - Pu_3S_4	Body-Centered Cubic	$I\bar{4}3d(T_d^6)$	8.4543±0.0005	-	4	8.41 - 9.28
Pu_2O_2S	Hexagonal	$C\bar{3}m$	3.927±0.003	6.769±0.010	1	9.95
PuOSe[142]	Tetragonal	-	4.151±0.003	8.369±0.005	-	7.69
PuTe[5]	Face-Centered Cubic	Fm3m	6.183±0.004	-	4	10.33

*Data from Zachariasen,[141] except as noted.

Efforts to prepare plutonium selenide by an analogous procedure resulted in a compound which was identified by Zachariasen as the oxyselenide, PuOSe.[142]

X-ray data on these compounds are listed in Table 2.44.

2-13 OTHER COMPOUNDS OF PLUTONIUM

A number of other plutonium compounds have been reported (see, for example, Chap. 10 in Ref. 20); in many cases, however, they have not been positively identified, and their postulated compositions have been based on analogy, inference, or conjecture. Such compounds will not be discussed here. There are, however, several classes of compounds that have been identified positively, and are worthy of inclusion; they are described below.

2-13.1 Plutonium Alkoxides. When a suspension of dipyridinium hexachloroplutonium (IV), $(C_5H_6N)_2PuCl_6$, in a 3:2 mixture of isopropyl alcohol and benzene was treated with ammonia, plutonium tetraisopropoxide, $Pu[OCH(CH_3)_2]_4$ was formed.[144] The product was soluble; however, evaporation of the solution produced the solid, grass-green compound. Upon recrystallization from isopropyl alcohol, the emerald-green solvated compound, $Pu[OCH(CH_3)_2]_4 \cdot (CH_3)_2CHOH$, was formed. Under a pressure of 0.05 millimeters, plutonium tetraisopropoxide sublimed at 220°; it appeared to be stable in dry air but very easily hydrolyzed in the presence of moisture.

Alcohol exchange with tert.-butyl alcohol and with 3-ethylpentand-3 gave products which were believed to be the corresponding alkoxides, but which were not identified.

2-13.2 Sodium Plutonyl (VI) Acetate. Sodium plutonyl (VI) acetate, $NaPuO_2(C_2H_3O_2)_3$, is one of the very few stable compounds of hexavalent plutonium. It may be prepared by the addition of sodium acetate and sodium nitrate to a solution of plutonyl (VI) in 0.2 molar nitric acid-0.9 molar acetic acid-0.1 molar sodium dichromate such that the final solution is five molar in sodium ions, 0.6 molar in acetic acid, and 0.2 molar in acetate ion.[145] Precipitation requires about two hours.

Sodium plutonyl (VI) acetate is a pink compound, and has a cubic structure with four formula units per unit cell.[146] Its space group is $P2_13(T^4)$ and the lattice constant, a_o = 10.664±0.002A. The calculated density of the compound is 2.578 grams per cubic centimeter.[146]

The solubility of $NaPuO_2(C_2H_3O_2)_3$ in water varies from six grams of plutonium per liter at 5° to 19 grams per liter at 95°.[145] In 0.6 molar acetic acid-0.2 molar sodium acetate solutions containing various concentrations of sodium nitrate, the solubility of $NaPuO_2(C_2H_3O_2)_3$, expressed as grams of plutonium per liter, decreases from 1.0 for a 0.8 molar $NaNO_3$ solution, to 0.070 for a solution 5.7 molar in sodium nitrate.

2-13.3 Plutonium Salicylates. Zvyagintsev and Sudarikov[147] have made a thorough study of the salicylates of plutonium. Upon addition of salicylic acid to a solution of plutonium (III), precipitation of a light blue, needle-like salicylate takes place at a pH of 0-1 and above. Chemical analysis revealed the precipitate to be $Pu(C_7H_5O_3)_3 \cdot 1.5H_2O$; its solubility as a function of salicylate ion concentration is give in Table 2.45.

On standing in air or under water for several days, the trivalent salicylate is oxidized to the plutonium (IV) salicylate, the oxidant apparently being dissolved at atmospheric oxygen. The trivalent salicylate dissolves in ammonia or alkali to form a salicylate complex of plutonium (IV), namely $[PuO(C_7H_4O_3)_2]^-$.

Addition of salicylic acid to a weakly acidic (pH of 0-1 or above) plutonium (IV) solution produces a flocculent, cocoa-brown precipitate that has been identified chemically as a salicylate of plutonium (IV), $PuO(C_7H_5O_3)_2$. As can be seen from Table 2.46, the solubility of this precipitate is lowest for low excess salicylate ion concentrations; higher concentrations dissolve the compound due to complex formation. In the presence of 20 grams per liter

Table 2.45 - SOLUBILITY OF PLUTONIUM (III) SALICYLATE AT pH OF 3.5 AND TEMPERATURE OF 20°[147]

Final Salicylate Ion Conc., g/liter	Plutonium (III) Salicylate Solubility, as mg plutonium/liter
27	140.0
50	45.0
77	7.0
90	3.5
120	2.0

Table 2.46 - SOLUBILITY OF PLUTONIUM (IV) SALICYLATE AT pH OF 4.5 AND TEMPERATURE OF 20°[147]

Final Salicylate Ion Conc., g/liter	Plutonium (IV) Salicylate Solubility, as mg plutonium/liter
50	5.4
100	12.0
120	14.0
200	23.2
300	40.0

of excess salicylate, the solubility of the precipitate decreases from 120 milligrams (as plutonium) per liter at a pH of 1.8, to five milligrams per liter at pH 4.2. The solubility of plutonium (IV) salicylate in dilute hydrochloric acid solutions is listed in Table 2.47.

Plutonium (IV) salicylate is soluble in ethyl alcohol, ether, acetone, and amyl acetate, yielding an orange-brown solution, but it is insoluble in chloroform and carbon tetrachloride. It is soluble in saturated ammonium carbonate solutions, due to formation of a complex carbonate, but is decomposed by concentrated acid or alkali. The salicylate is soluble in alkaline solutions of sodium or ammonium salicylate with the formation of a salicylate complex; the resulting solution is unstable on heating and hydrolyzes to form a yellow or brown precipitate, whose composition is not yet known with certainty, but is thought to be $PuO_2 \cdot Pu(C_7H_5O_3)_2 \cdot xH_2O$.

2-13.4 Perovskite-Type Compounds of Plutonium. Several plutonium compounds of formula ABO_3 and having the perovskite structure have been prepared and studied by Russell, Harrison, and Brett.[148] Two types of compounds were made: $Pu^{3+}B^{3+}O_3$, where B is Al, V, Cr, or Mn, and $A^{2+}Pu^{4+}O_3$, where A is Ba. X-ray crystallographic data for these compounds appear in Table 2.48.

Plutonium aluminate, $PuAlO_3$, was first prepared inadvertently when a pelletized mixture of plutonium dioxide and graphite was heated in an alumina boat in an argon atmosphere for two hours at 1500°. Apparently the PuO_2 was reduced to Pu_2O_3, which then reacted with the alumina. It was later made by sintering pelletized mixtures of PuO_2 and $Al(OH)_3$ in hydrogen or argon at 1500° for two hours. The X-ray patterns differed somewhat with the method of preparation, suggesting that the product has a variable composition.

Plutonium vanadate, $PuVO_3$, was prepared by sintering compacted mixtures of PuO_2 and V_2O_5 in hydrogen for two hours at 1500°.

Table 2.47 - SOLUBILITY OF PLUTONIUM (IV) SALICYLATE IN DILUTE HYDROCHLORIC ACID AT 25°[147]

pH of Solution	Plutonium (IV) Salicylate Solubility, as mg plutonium/liter
5.7	0.3
5.2	0.5
3.0	1.3
2.0	6.2
1.5	50.0
0.4	71.0

Table 2.48 - X-RAY CRYSTALLOGRAPHIC DATA FOR PEROVSKITE-TYPE COMPOUNDS OF PLUTONIUM[148]

Compound	Symmetry	Lattice Constants, A a_o	b_o	c_o	Calculated Density, g/cm^3
$PuAlO_3$	Rhombohedral	5.33 $\alpha = 56^o4'$			9.28
$PuVO_3$	Orthorhombic	5.48	5.61	7.78	9.41
$PuCrO_3$	Orthorhombic	5.46	5.51	7.76	9.65
$PuMnO_3$	Pseudo-Cubic(?)	3.86			9.89
$BaPuO_3$	Cubic	4.39			8.3

The compound $PuCrO_3$ was formed when pelletized mixtures of PuO_2 and CrO_3 were sintered in thoria crucibles for two hours at 1500° in hydrogen. Use of an alumina crucible resulted in $PuAlO_3$ instead of $PuCrO_3$. Apparently $PuMnO_3$ was prepared by sintering compacted PuO_2-$MnCO_3$ mixtures in hydrogen for two hours at 1500°, but its structure has not been resolved.

While the above compounds containing plutonium (III) were prepared under reducing conditions, the production of $BaPuO_3$, in which plutonium is tetravalent, required oxidizing conditions. Compacted mixtures of PuO_2 and 10 percent excess $BaCO_3$ heated at 1650° for three hours produced the highest yields of $BaPuO_3$, although the compound may be prepared under less rigorous conditions (2 hours at 1500°).

The physical and chemical properties of these compounds have not been investigated, but apparently all have melting points above 1500°. At least one of them, $BaPuO_3$, is stable in oxidizing atmospheres up to 1500°. With the exception of $PuMnO_3$, all have low neutron absorption cross sections. This factor, in addition to the good irradiation stability of cubic oxides in general, prompted the authors[148] to suggest the possible use of these compounds as reactor fuels. Their low plutonium density, however, makes it highly unlikely that they will ever be suitable for this purpose.

Attempts to prepare $PuFeO_3$, $PuGaO_3$, $MgPuO_3$, $CdPuO_3$, $PbPuO_3$, $BePuO_3$, $CaPuO_3$, $SrPuO_3$, and $KPuO_3$ by the above techniques were unsuccessful.

2-13.5 Miscellaneous Compounds of Plutonium. Plutonium (IV) acetylacetonate, $Pu(C_5H_7O_2)_4$, a red-brown crystalline compound, was precipitated by the addition of an ammonium hydroxide solution to a plutonium (IV) sulfate solution, followed by addition of enough ammonium hydroxide to render the solution alkaline.[149] It has a vapor pressure of approximately 1.5×10^{-4} millimeters at 140°, and melts at 170 - 173°. The acetylacetonate is very soluble in benzene.

Plutonium (IV) 8-hydroxyquinolate, $Pu(C_9H_9NO)_4$, has been prepared as a dark red-brown precipitate by the addition of 8-hydroxyquinoline to a dilute solution of plutonium (IV) in acetic acid-sodium acetate at pH 3-5.[150] Its solubility in this solution is reported as 77 milligrams per liter. Plutonium (VI) forms an orange-brown precipitate with 8-hydroxyquinoline.

Potassium ferricyanide, $K_3Fe(CN)_6$, forms insoluble compounds with plutonium (III), (IV), and (VI), as does potassium ferrocyanide, $K_4Fe(CN)_6$, with plutonium (III) and (IV).[151] The precipitates are formed by adding the appropriate potassium compound to a solution of plutonium in the proper oxidation state in dilute acid. The formulas and some of the properties of the resulting compounds are shown in Table 2.49.

In each case the approximate composition has been established by chemical analysis, although the exact degree of hydration is not known with certainty.

There are numerous other insoluble compounds of plutonium with organic reagents. Thus tetravalent plutonium forms precipitates with benzoic acid (green-yellow), m-nitrobenzoic acid (pale green), n-propylarsonic acid (pale green), phenylarsonic acid (pale green), p-dimethylaminobenzeneazophenylarsonic acid (orange), 3-nitro-4-hydroxyphenylarsonic acid (pale green), p-dimethylaminobenzeneazophenylarsinic acid (orange), m-nitrophenylarsonic acid (pale green), sebacic acid, dihydroxytartaric acid, phthalic acid, thiobarbituric acid, and sodium benzene-sulfinate (buff). Plutonium (III) does not form precipitates with any of these compounds; this difference in behavior was once utilized in laboratory separations, but now most of these materials are relatively little-known and little-used. In fact, the exact compositions of most of the above precipitates are not known with certainty.

Table 2.49 - PLUTONIUM FERROCYANIDES AND FERRICYANIDES[151]

Compound	Oxidation State of Plutonium	Oxidation State of Iron	Color	Solubility, g Plutonium/liter
$HPuFe(CN)_6 \cdot 7H_2O$	3	2	Sky blue	0.0088
$PuFe(CN)_6 \cdot 7H_2O$	3	3	Black	0.012
$PuFe(CN)_6 \cdot 3.5H_2O$	4	2	Black	10
$Pu_3[Fe(CN)_6]_4 \cdot 15H_2O$	4	3	Black	7.5
$(PuO_2)_3[Fe(CN)_6]_2 \cdot xH_2O$	6	3	Red-brown	0.40

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