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Plutonium Hexafluoride, Plutonium (VI) Oxyfluoride: Preparation, Identification, and Some Properties

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The x-ray diffraction data for plutonium and uranium compounds were obtained by Finley H. Ellinger of the Chemistry-Metallurgy Division, Group CMR-5 of this laboratory.

The sin $^{2}\theta$ values for neptunium hexafluoride are unpublished values which were supplied by F. W. H. Zachariasen of the Argonne National Laboratory.

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I Introduction:

Early in the history of the Plutonium Project consideration was given to the possible use of a volatile plutonium compound as a means of isolating and purifying the pile-produced plutonium. From the similarities between the chemistry of plutonium and uranium it was deduced that plutonium hexafluoride should have properties comparable to the highly volatile uranium hexafluoride. Studies at that time with tracer quantities of plutonium produced contradictory results, but it was found that if fluorine gas was passed over a plutonium compound at about 500°C the plutonium distilled from the hot zone and deposited in cooler zones. Brown and Hill (1), using microgram quantities of plutonium in a series of distillation experiments with uranium hexafluoride, concluded that the higher fluoride of plutonium is unstable in the absence of fluorine and decomposes to plutonium tetrafluoride over a period of hours at room temperature. They also concluded that the vapor pressure of the plutonium compound was about the same as that of uranium hexafluoride. Davidson, Katz, and Orlemann (2) conducted experiments in which plutonium was volatilized from a nickel filament in an atmosphere of fluorine directly onto a cold platinum surface. The plutonium deposited at temperatures as high as room temperature and did not redistill at temperatures as high as 200°C, indicating that the compound was not volatile at this temperature or had been converted to a non-volatile compound.

[redacted]

At a later date, the problem was reinvestigated using milligram quantities of plutonium. In general, the results of this work were as inconclusive and difficult to explain as the early experiments. However, some experiments by Fisher, Vaslow, and Tevebaugh (3) seemed to indicate that the higher fluoride has a negative heat of formation and is stable only at high temperatures in an atmosphere of fluorine. Their tentative conclusion was that the higher fluoride might be condensed rapidly to a point where the rate of decomposition would be low, but on heating to revolatilize, the compound would be expected to decompose even in a stream of fluorine unless the temperatures were raised to 350 to 550°C. Florin (4) prepared a volatile compound of plutonium which was presumed to be plutonium hexafluoride, although it decomposed before its identity could be established. In this experiment the volatile material was condensed on a glass surface at low temperature and after a few minutes' aging, the compound became less volatile and changed from solid to liquid. This behavior was interpreted as evidence of reaction of the fluoride with the glass surface.

No further experimental work on this problem has been reported, although the preparation of neptunium hexafluoride (5, 6) has been achieved.

Brewer, Bromley, Gilles, and Lofgrin (7, 8) made use of existing thermodynamic data plus reasonable estimates of other data, based principally on the relationship between the behavior of corresponding

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plutonium and uranium compounds, to predict the properties of plutonium hexafluoride. They concluded that all the lower fluorides, including the yet unisolated plutonium pentafluoride, would be oxidized to plutonium hexafluoride by an atmosphere of fluorine at all "reasonable temperatures." Also, it was predicted that plutonium hexafluoride would be gaseous and have a boiling point slightly above room temperature. On the basis of their predictions, admittedly based on questionable data, they proceeded to make detailed and stimulating suggestions as to possible methods of preparation.

At the present time a study of the preparation and properties of plutonium hexafluoride is in progress at this laboratory. The present report represents the progress to date. Additional information will be reported as it becomes available.

II Apparatus and Experimental Procedure

The general scheme selected for the preparation of plutonium hexafluoride provides for the passage of fluorine gas over hot plutonium tetrafluoride. Any volatile reaction product is removed in a liquid oxygen trap down stream from the reactor.

The auxiliary equipment leading to and from the reactor and its associated traps and storage vessels has been modified but slightly during the course of the investigation. The schematic diagram for this apparatus is shown in Figure 1. The materials of construction are nickel, brass, copper, and fluorocarbon plastics. Connections between the parts are made with flare fittings or are silver soldered. Valves which have been used successfully include Kerotest (brass

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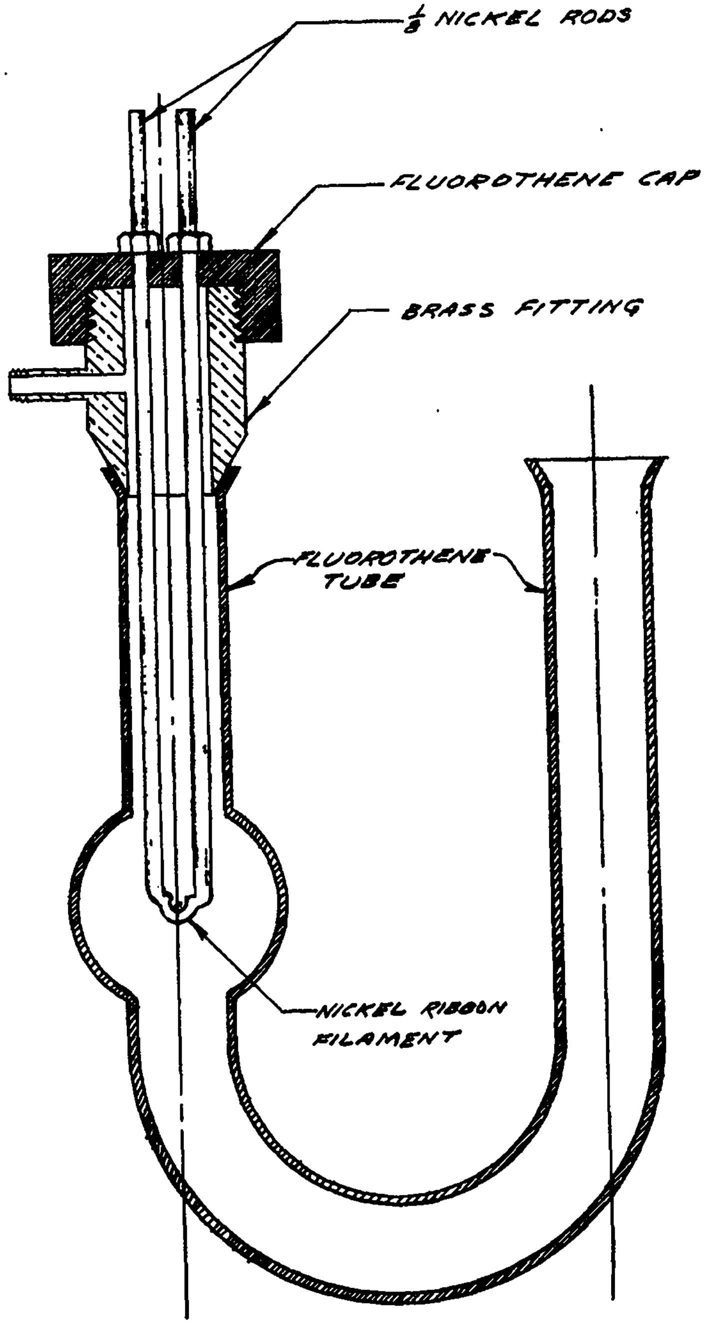

FLUOROTHENE REACTOR
FIGURE 2

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angle valves packed with Teflon plastic turnings), weinstock needle valves (Teflon packed, monel stems) and Hoke, brass-bellows, needle valves. In operation, fluorine from a storage tank is passed through a liquid oxygen trap containing potassium fluoride to remove hydrogen fluoride and then through the manifold into the reaction chamber. Volatile reaction products are removed in a suitable liquid oxygen trap and fluorine passes on through the trap into a calcium chloride tube where chlorine is liberated. The chlorine is prevented from entering the vacuum pump which follows by a liquid nitrogen trap. All customary precautions for cleaning the apparatus in which fluorine is to be used have been observed. Previous to a preparation the apparatus is thoroughly degassed and then fluorinated at an elevated temperature.

Initially the reactor and accompanying storage chambers were constructed of glass. There followed a similar apparatus constructed of Fluorothene plastic. It consisted mainly of a series of Fluorothene U tubes, see Figure 1, which could be isolated by Fluorothene stopcocks or Fluorothene needle valves. The first U tube served as the reactor, Figure 2. In the reactor, a nickel strip filament, with a cup-like depression in its center for holding the material to be fluorinated, was strung across a pair of nickel rods which entered the reactor through a Fluorothene cap. To prepare plutonium hexafluoride, a load of plutonium tetrafluoride was placed on the filament, fluorine was admitted to the reactor, and the filament was

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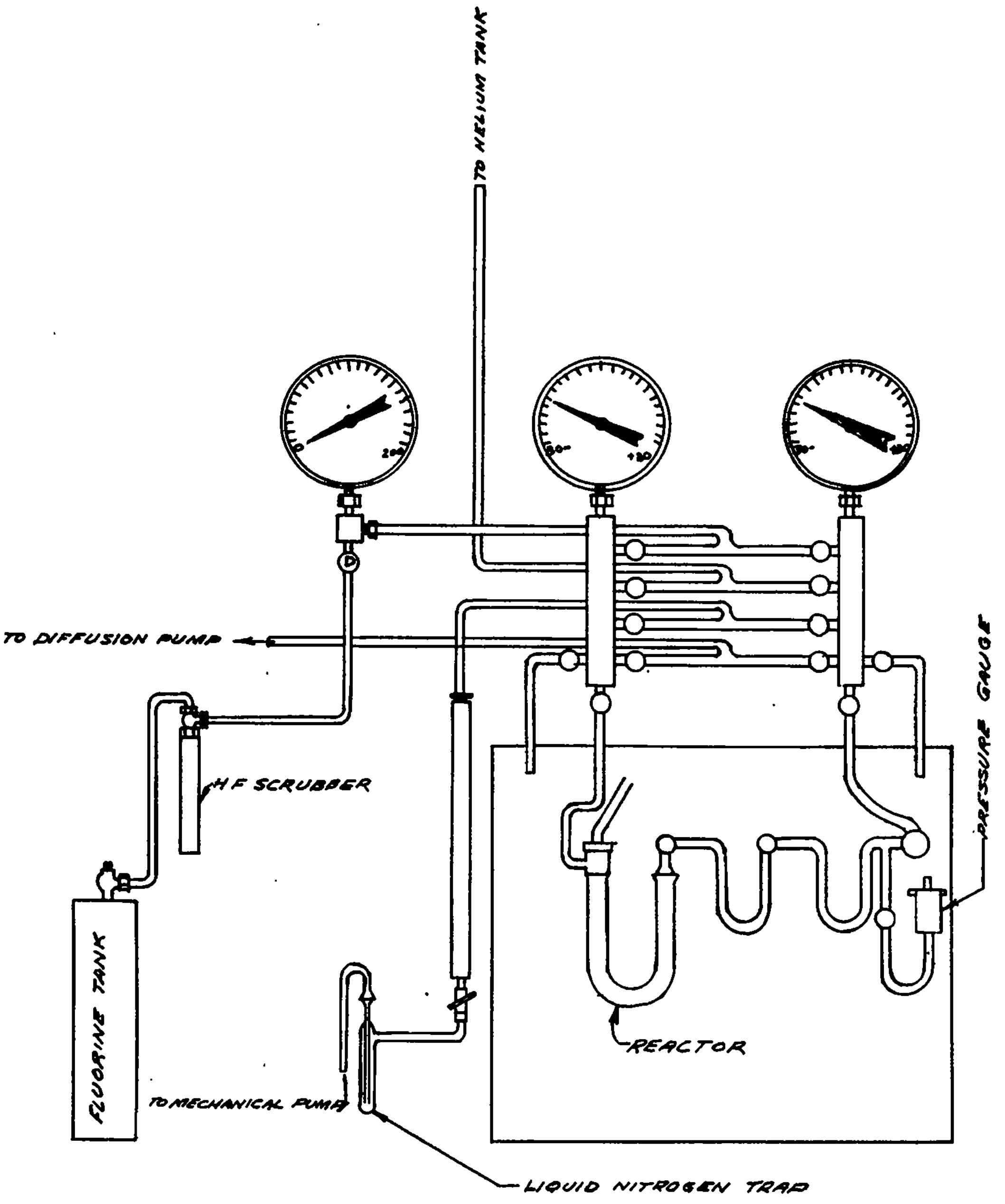

FLUORINATION APPARATUS
FIGURE 1

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heated electrically to the temperature required for the reaction. The reactor was cooled in liquid oxygen both to prevent thermal decomposition of the Fluorothene tube by heat from the filament and to provide a cold surface for condensation of the volatile reaction products. Liquid oxygen was used as the refrigerant rather than less hazardous liquid nitrogen, because the boiling point of fluorine is lower then that of oxygen but higher than that of nitrogen. Plutonium hexafluoride, which collected on the walls of the reactor during the course of the reaction, was sublimed from the reactor, condensed into one of the U tubes which followed the reactor, and sealed off by closing valves or stopcocks. By distilling and condensing the product at various temperatures its volatility and stability could be observed qualitatively.

In order to obtain a sample of plutonium hexafluoride mounted in a capillary for x-ray diffraction analysis, the simple apparatus described above was modified to the extent of including a short glass T in the line. The free side of the T was drawn to a capillary which could be sealed off after the sample was sublimed into it. As was previously observed plutonium hexafluoride decomposed rapidly on contact with glass, but in this instance it was possible to preserve a sample in the capillary after a protective coating of decomposition product had built up on the walls of the capillary.

Another modification of the simple apparatus permitted a measurement of the vapor pressure of plutonium hexafluoride. A U trap and

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pressure gauge were connected to the line by means of a T fitting, and a valve at the T permitted the gauge and trap to be isolated from the line. Plutonium hexafluoride could be sublimed into the U trap, the valve closed, and the vapor pressure measured at various temperatures by the pressure gauge attached to the trap. The pressure gauge, Figure 3, was of the null-point diaphragm type; the exposed parts were made of Fluorothene plastic with the exception of the diaphragm itself which was a thin sheet of Teflon plastic. The plastic parts were mounted in a metal housing through which external pressure could be applied as necessary to balance the diaphragm to null position. The balancing external pressure was then equal to the vapor pressure of plutonium hexafluoride inside the gauge, and its magnitude could be read from a mercury manometer connected to the external pressure system. Actually the pressure balancing was performed automatically and continuously in the following way. The outer side of the diaphragm was coated with Aquadag, a graphite suspension, and grounded to become one plate of a condenser. The other plate of the condenser was a metal disc mounted above the diaphragm and connected by a wire to the sensitive post of a Niagara Electron Laboratories, Thermocap relay. Changes in capacity of the condenser brought about by changes in position of the diaphragm caused the Thermocap relay to actuate magnetic valves to increase or decrease the external pressure as necessary to restore the diaphragm to the null position.

More recently the reactor and auxiliary apparatus have been

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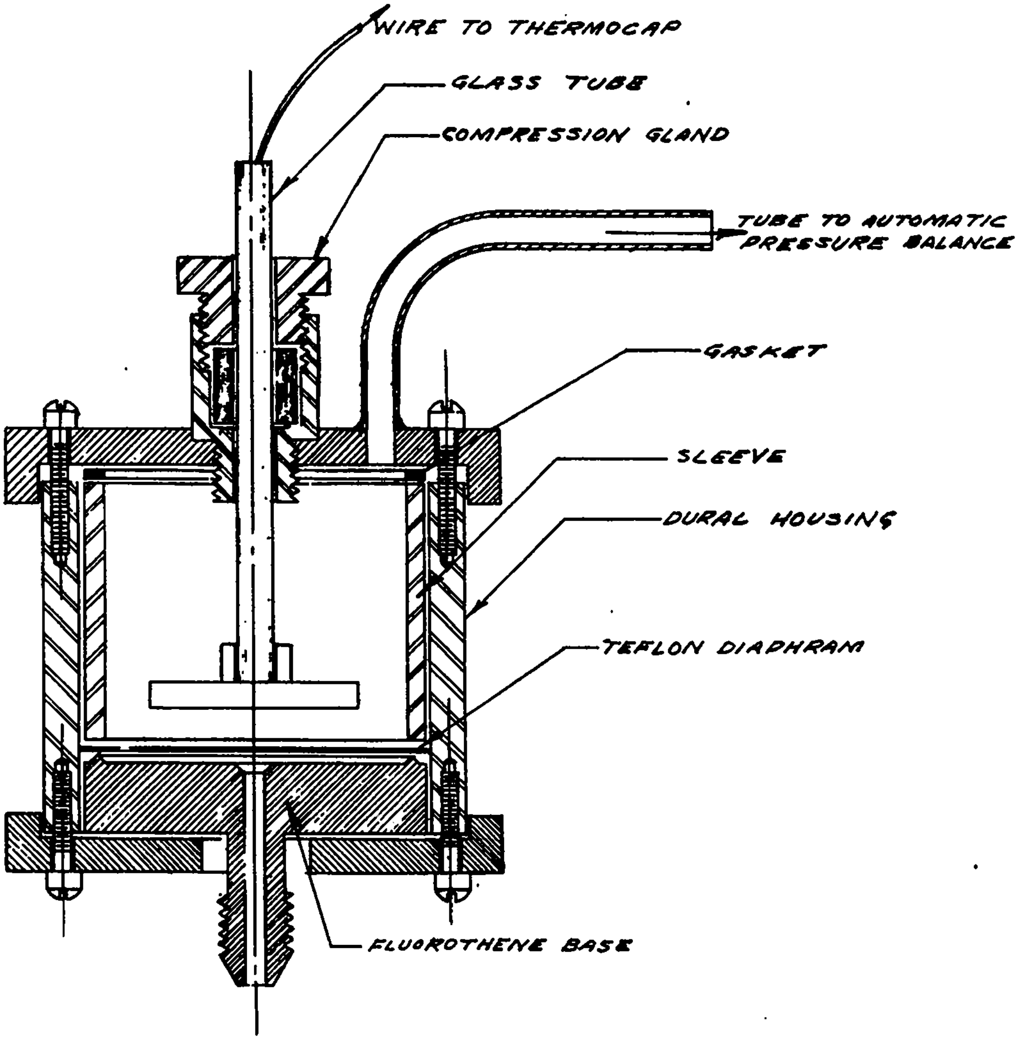

FLUOROTHENE PRESSURE GAUGE

FIGURE 3

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constructed of nickel, copper, and brass with silver soldered or welded joints. The reactor, see Figure 4, consists of a nickel tube in which a nickel boat containing the plutonium tetrafluoride is placed. A wire wound furnace is used to heat the boat as fluorine is passed over it. The reaction product is condensed in a trap cooled with liquid oxygen. Later the volatile product is transferred to a metal manifold system consisting of three nickel cylinders (25 ml volume), a fluorothene tube (¼ in. diameter) with closed end, a Bourdon tube pressure gauge, and a sensitive pressure gauge all connected by needle valves to a nickel manifold. The manifold also has a valve leading to a vacuum source. One of the nickel cylinders is a storage vessel for plutonium hexafluoride, another contains potassium fluoride for removing hydrogen fluoride from the plutonium hexafluoride, and the third is a trap into which any volatile impurities may be distilled. The fluorothene tube permits visual observation of the product. The sensitive pressure gauge assembly is of the Booth-Cromer (9) type. It is a mull-point, diaphragm type gauge of nickel construction. An electronic device senses the position of the diaphragm and automatically causes a balancing of the pressure external to the system. A mercury manometer indicates the balancing pressure and consequently the pressure in the system. A small copper U tube placed between the gauge and the valve attached to the manifold holds the sample for which the vapor pressure is to be determined. The tube is thermostated at the temperature at which the pressure is to be

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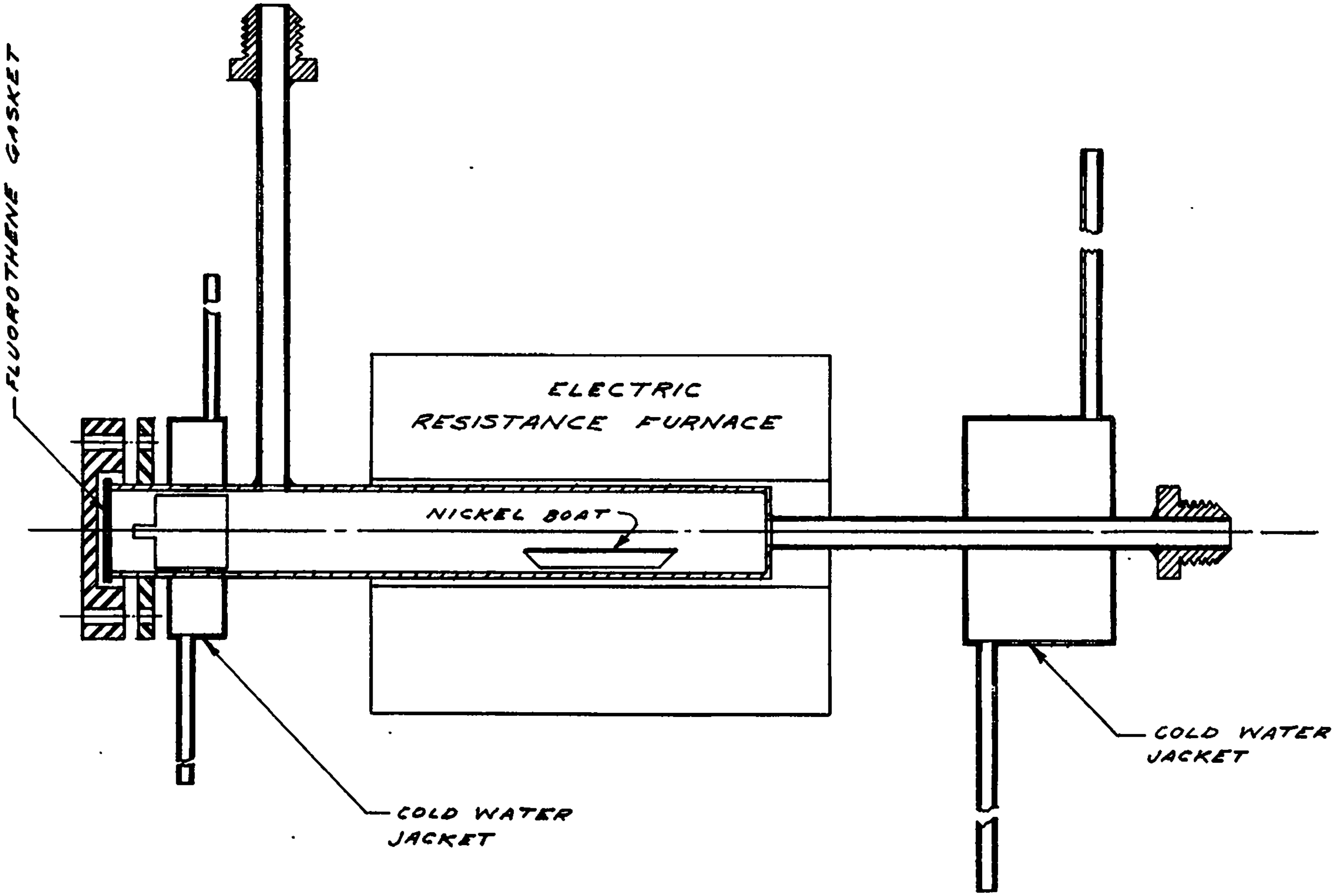

NICKEL REACTOR

FIGURE 4

[redacted]

measured, and the gauge is maintained at a slightly higher temperature.

III The Reaction Between Plutonium Tetrafluoride and Fluorine

During the course of this investigation over 1 g of plutonium hexafluoride has been prepared by the action of fluorine on plutonium tetrafluoride. Quantities prepared in any given batch have ranged from a few milligrams to approximately 0.5 g. A reaction temperature between 600 and 700° was found to be most suitable, although the reaction rate is an order of magnitude slower than the analogous reaction between uranium tetrafluoride and fluorine. At a temperature of about 400°, where uranium tetrafluoride and fluorine react rapidly, the reaction rate for the plutonium compound is diminished to a negligible value. Attempts to speed the reaction by employing temperatures of 800 to 1000°C resulted in fusion of the surface of the plutonium tetrafluoride with a consequent reduction in the reaction rate. In one experiment plutonium trifluoride was used in the hope that a higher temperature could be reached before fusion occurred. In this experiment the plutonium trifluoride ignited in the fluorine at a relatively low temperature. Very little volatile product was formed, and the fused residue appeared to be plutonium tetrafluoride.

The cause for the slow reaction rate is not known, but apparently it is not due to impurities in the plutonium tetrafluoride or to its state of division. There is some crude evidence that an unfavorable equilibrium may be responsible for the slow rate. More plutonium tetrafluoride disappeared (presumably as plutonium hexafluoride) from

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the reactor at the higher rates of fluorine flow than for the smaller rates, even though a thirty fold excess of fluorine was used for the lowest flow rate. With a fluorine flow of 1 millimole per minute about 0.01 millimole per minute of plutonium tetrafluoride was consumed. With a flow rate of 0.1 millimole per minute only 0.0033 millimole per minute of plutonium tetrafluoride was consumed. Unfortunately it is not certain that plutonium tetrafluoride consumption is equivalent to plutonium hexafluoride production, since only 60% of the tetrafluoride consumed is collected in the cold trap as hexafluoride.

In a recent preparation, very large crystals of plutonium tetrafluoride were formed on a flat extension of the nickel boat in a direction down stream with respect to fluorine flow. The mechanism for this crystal growth has not been determined.

IV Characterization and Identification of Plutonium Hexafluoride

A. X-ray Pattern:

The identification of plutonium hexafluoride is based on a single x-ray diffraction pattern. Only a weak pattern was obtained, but it indicated clearly that the plutonium compound was isomorphous with both uranium hexafluoride and neptunium hexafluoride. The data indicate that plutonium hexafluoride has a slightly smaller unit cell size than uranium hexafluoride, as would be expected from an actinide contraction effect. A comparison of the x-ray diffraction patterns for plutonium, uranium, and neptunium hexafluorides is given in

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Table I. The UF_6 structure was solved by Hoard and Stroupe (10. They found that UF_6 is orthorhombic with the D_{2h}^{16}-Pnma space group. The lattice constants are: $a_o = 9.95$ Å, $b_o = 9.02$ Å, $c_o = 5.26$ Å.

Table I

A Comparison of X-Ray Diffraction Patterns For
Plutonium, Uranium, and Neptunium Hexafluorides

PuF_6		UF_6		NpF_6	
$\sin^2\theta$	Intensity	$\sin^2\theta$	Intensity	$\sin^2\theta$	Intensity
		.0223	w	.0224	vvw
				.0279	vw
.0294	mw	.0293	w	.0290	s
.0317	mw	.0315	w	.0319	s
.0354	mw	.0352	w	.0353	s
				.0463	w+
.0577	w	.0574	w	.0575	s-
.0760	w	.0757	w	.0764	m+
.0842	vw	.0834	w	.0838	w
.0912	w	.0908	w	.0904	w+
.0944	vw			.0956	w-
.1005	vw			.1008	w
.1062	w			.1062	w+
				.1124	vw
.1178	vw			.1184	w
.1265	w	.1265	w	.1261	w
		.1343	w		
.1428	w	.1420	w	.1431	w+
.2104	w				
.2398	w	.2384	w		
.2632	vw				
.3035	w				
.3394	vw	.3385	vw		
.3589	vw	.3560	vw		
		.3855	vw		

All patterns were obtained with copper $K\alpha$-radiation

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B. Physical Appearance:

Freshly condensed plutonium hexafluoride is light brown in color and is finely crystalline. On standing at room temperature the crystals increase in size and the color deapens to a red-brown.

No liquid phase has yet been observed. Attempts to determine the melting point have been unsuccessful due to the complete volatilization of the compound before the melting temperature could be reached.

C. Vapor Pressure:

The vapor pressure of plutonium hexafluoride was measured at several points in the range -83° to 23.3°C. Although a breakdown of the apparatus prevented a second determination, a reasonable degree of confidence is held in the results of the one experiment. The vapor pressure of plutonium hexafluoride has been found to be almost identical to that of uranium hexafluoride within experimental error over the temperature range investigated. The data are shown in Table II. A slight solid residue found in the apparatus at the completion of the experiment gave evidence that some decomposition of plutonium hexafluoride had occurred during the time the measurements were being made.

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Table II

Comparison of the Vapor Pressure for Plutonium and Uranium Hexafluorides

Temperature °C	Vapor Pressure (mm of mercury)	
	PuF_6	UF_6*
-83	0	2.8×10^{-3}
-11	14	7.7
0	24	17
16	63	59
20.3	83	81
23.3	102	98

* Values for the vapor pressure of uranium hexafluoride are from the report A-753 by J. Kirshenbaum.

D. Stability and Radiodecomposition

While attempts were being made to measure the vapor pressure of plutonium hexafluoride, it was observed that the pressure increased slowly with time, although the temperature was held at 0° and the apparatus was known to be free of leaks. This slow pressure increase with time at constant temperature was also observed at higher temperatures. The rate of pressure increase was nearly independent of temperature, although at each new higher temperature there was an initial rapid pressure rise which tapered off to the constant slow rate after a number of hours. It is presumed that the initial rapid rate resulted from degassing of the solid compound mass and was not evidence for decomposition at an increased rate.

The steady pressure increase appears to be due to the decomposition of plutonium hexafluoride to fluorine gas and a plutonium fluoride of lower oxidation number. The observed decomposition rate

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is subject to great uncertainty since the sample weight must be estimated visually; however, a rate of 3 or 4% per day is indicated. This decomposition does not necessarily imply thermodynamic instability of plutonium hexafluoride, since a calculation shows that the decomposition that could be caused by the alpha particle radiation of plutonium would cause a pressure increase of the order of magnitude that has been observed. If it is assumed that 30 electron volts are required to break a bond, and no allowance is made for possible recombination or for the possible effects of geometry, a decomposition rate of 1.3% per day is obtained.

From the weight of solid residue resulting from the decomposition of plutonium hexafluoride over an extended period of time, the half-life for decomposition was fixed at not greater than 80 days. For an 80 day half-life the decomposition would be 0.86% per day.

From these three estimates of the decomposition rate it is probable that the decomposition rate lies between 1% and 4% per day. Insufficient data are available to determine conclusively the question of thermal stability.

The solid compound resulting from the decomposition of plutonium hexafluoride has not yet been identified.

V Stability of Plutonium Hexafluoride in Contact With Certain Materials for Construction of Apparatus

With sizable quantities of plutonium hexafluoride available, it became practical to study quantitatively the relative stability of

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the compound with respect to the various materials which might be considered practical for the construction of apparatus for its handling and storage. Results were obtained for the decomposition of gaseous plutonium hexafluoride at room temperature on copper, nickel, platinum, silver solder, brass, and Fluorothene plastic.

Duplicate sets of thin strips of the various materials were suspended from nickel wires in two nickel vessels. The strips were first conditioned by heating to 100° in fluorine; then plutonium hexafluoride was distilled into the nickel vessels and the vessels closed off and allowed to stand at room temperature. After 8½ hours the plutonium hexafluoride was evacuated from one vessel, and the strips were removed, weighed, and washed in nitric acid to remove any plutonium which may have deposited on them. The wash solutions from various strips were then assayed for plutonium by counting. The second set of strips was treated in the same way after being exposed to plutonium hexafluoride for 269 hours at room temperature.

The results are tabulated in Table III. Of the materials tested, nickel appears to be the best, with copper second, for prolonged exposure to plutonium hexafluoride at room temperature; however, platinum appears to be better for exposures of less than 8½ hours. The rate of attack diminishes considerably with increasing exposure time except in the case of Fluorothene on which plutonium was deposited in amounts nearly proportion to the time of exposure. Also the plutonium appeared to soak into the Fluorothene so that it could not be

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removed completely by washing in acid.

Visual inspection of the test strips revealed little change of appearance except in the case of silver solder which had turned almost black on exposure to fluorine and turned still darker on exposure to plutonium hexafluoride. However, tiny scratches not covered by the black coating were present. The presence of these uncorroded scratches is assumed to be related to the method of preparation of the test strips. Prior to exposure to plutonium hexafluoride, the silver solder strips were cleaned in nitric acid. This treatment produced a quite soft, whitish bloom on the strips. This bloom was not polished off, but portions of it were scratched while handling the strips with metal forceps, and it is believed that these scratches are the same as the uncorroded scratches apparent after exposure to plutonium hexafluoride. If this interpretation is correct, the corrosion properties of a polished, silver-solder surface should be quite different and better than those observed for a surface which has been cleaned with nitric acid.

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Table III

Decomposition of Plutonium Hexafluoride on Various Materials

Material	8.5 hour Exposure		269 hour Exposure		Ratio of Pu Deposits**
	Wt. gain* (mg)	Pu Deposit ($\mu g/cm^2$)	Wt. gain* (mg)	Pu Deposit ($\mu g/cm^2$)	
Copper	0.3	4.2	0.46	9.4	2.24
Nickel	0.15	3.2	0.65	7.1	2.21
Platinum	0.1	2.3	0.55	9.1	3.94
Silver solder	0.3	55.5	1.60	230.0	4.14
Brass	0.2	5.5	0.5	26.7	4.85
Fluorothene	0.2	10.6	0.3	353.0	33.30

* The weight gains for the 8.5 hour exposure are somewhat uncertain because plastic caps used on the weighing vials suffered weight changes for which complete correction may not have been made.

** Ratio of 269 hour plutonium deposit to 8.5 hour deposit. The ratio of the exposure time is 31.6.

VI Plutonium(VI) Oxyfluoride

A residue obtained when plutonium hexafluoride was exposed to moist air was submitted for x-ray analysis. Only a very weak pattern was obtained, but the evidence is fair that the substance was plutonium(VI) oxyfluoride with the formula PuO_2F_2. In general, only the stronger lines of a pattern of uranium(VI) oxyfluoride, which was used for comparison, had counterparts in the pattern of the plutonium compound. In Table IV are recorded the values for the interplaner spacings, or "d" values, from the x-ray diffraction pattern, which could be measured for the plutonium compound, together with

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corresponding values for uranium(VI) oxyfluoride.

Table IV

A Comparison of "d" Values from the X-Ray Diffraction Pattern of Plutonium and Uranium Oxyfluorides

PuO_2F_2		UO_2F_2	
d	Intensity	d	Intensity
5.264	ms	5.184	m
3.502	ms	3.502	m
2.256	m		
2.077	m	2.091	s
1.939	w	1.941	s
1.781	vw	1.771	w
		1.797	w
1.629	vw	1.633	m
1.382	vw	1.365	w
1.348	vw	1.339	m
1.198	vw	1.211	m
1.174	vw	1.179	m
0.993	vvw	0.994	w
0.897	vw	0.899	w
		0.898	w

An additional phase was detected in the x-ray pattern of a residue resulting from decomposition of plutonium hexafluoride after long standing in the apparatus and probable exposure to moist air. Although its chemical composition is unknown, it was identified as the same phase as that obtained when hydrogen fluoride is passed over moist plutonium peroxide precipitates at temperatures below 400°.

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