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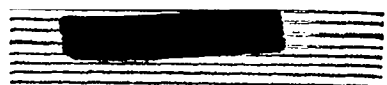
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LOS ALAMOS SCIENTIFIC LABORATORY

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Plutonium Hexafluoride: Second Report On The

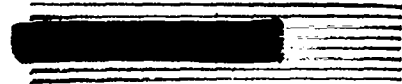
Preparation and Properties

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A. E. Florin

November 9, 1950

Chemistry-Transuranic Elements



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### Introduction

It is the purpose of this paper to present the results of experimental investigations on the chemistry of plutonium hexafluoride conducted at this laboratory subsequent to the preparation of report LAMS 1118(1). A more satisfactory apparatus for the preparation is described. More reliable values for the vapor pressure have been obtained and the related physical constants have been calculated. The rate of decomposition of the compound as a result of the associated alpha radiation has been determined and a preliminary observation on the thermal stability is reported.

### Preparation of Plutonium Hexafluoride

As was stated in LAMS 1118, the reaction employed for the preparation of plutonium hexafluoride,  $\text{PuF}_4 + \text{F}_2 \rightarrow \text{PuF}_6$ , appears to be favored by a high rate of flow of fluorine over the hot plutonium tetrafluoride. Evidence will be presented elsewhere in this paper which indicates that this probably results from an unfavorable equilibrium at the temperature required for the reaction to take place.

The flow methods described previously for the preparation wasted large quantities of fluorine since no provision was made for recycling. A new reactor has been designed which eliminates this difficulty and is much simpler to operate. The reactor assembly is shown in Fig. 1. It consists of a vertical brass tube 5" high and 1-1/2" diameter, with a brass bottom silver soldered in place and a Teflon gasketed brass

  
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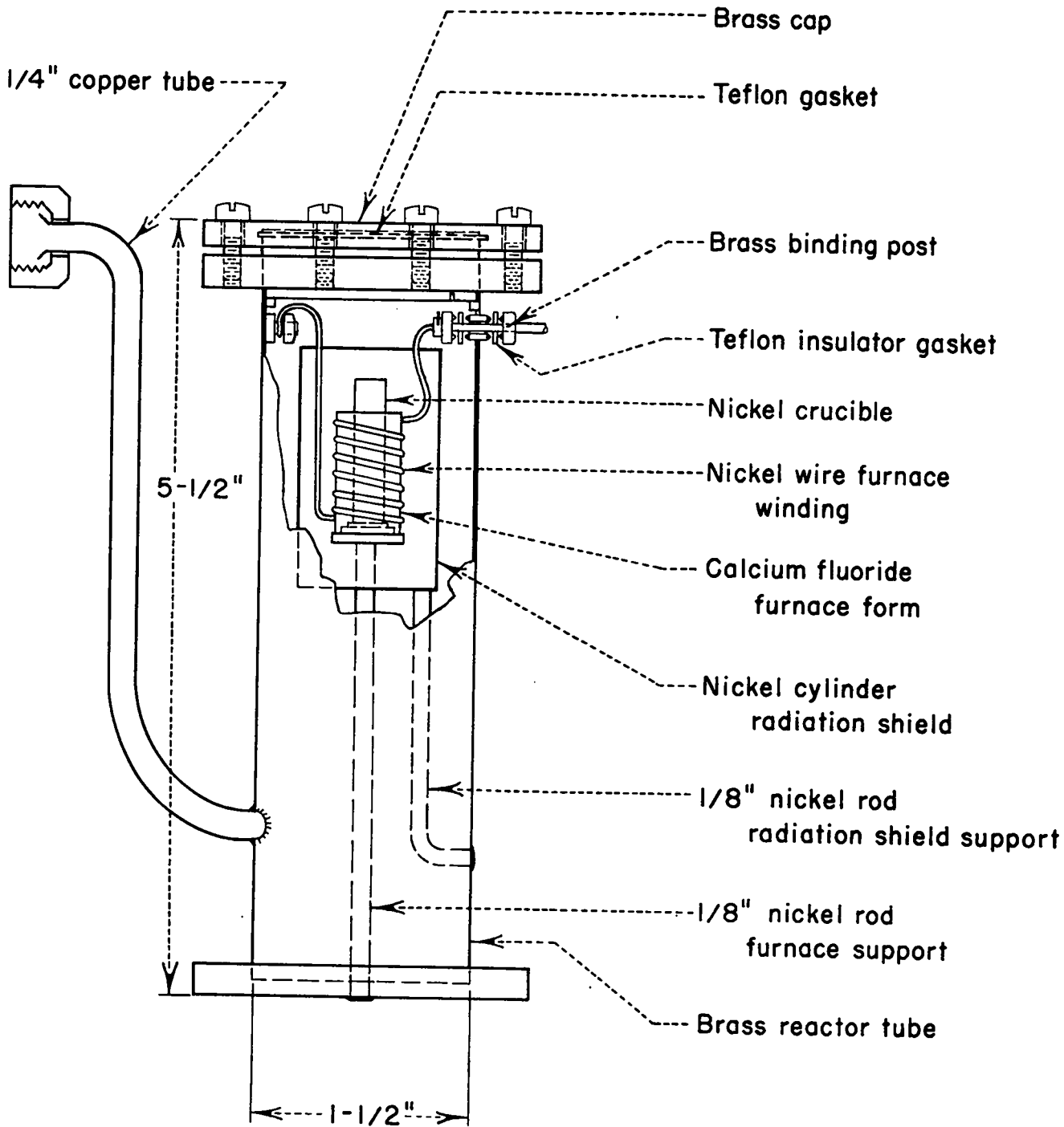
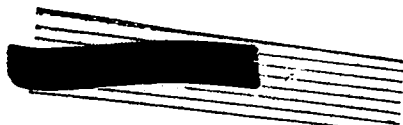


FIG. 1 FLUORINATION REACTOR



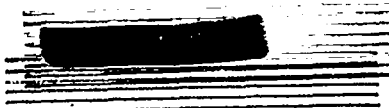



cap held on by six screws threaded into a flange on the reactor. Inside the reactor is a small resistance furnace consisting of 10 turns of 24 gauge nickel wire wound in a helical groove on a calcium fluoride tube\* 1" high, 5/8" O.D. and 13/32" I.D. A nickel crucible, 1-1/4" high, 3/8" O.D. and .035" wall thickness, fits inside the furnace and is used to hold the material to be fluorinated. A suitable size charge is 0.5g of plutonium tetrafluoride.

During a fluorination run the reactor is immersed in a dry ice-trichloroethylene bath, fluorine is admitted to a pressure of one atmosphere, and the furnace is heated electrically to a temperature of about 700°. The cold walls and the hot furnace presumably give rise to strong convection currents which provide circulation of the fluorine over the plutonium tetrafluoride in the crucible. The plutonium hexafluoride formed in the fluorination reaction is condensed out on the cold reactor wall, so that the reaction keeps going on a single charge of fluorine plus small amounts to compensate for that used up in the reaction. A production rate of approximately 40 milligrams of plutonium hexafluoride per hour has been realized in practice.

To reach a temperature of 700° in the crucible, it is necessary to have the nickel wire furnace at a temperature considerably higher than 700°. At this higher temperature the nickel wire is corroded by fluorine at an appreciable rate, and it was found necessary to replace

\*The calcium fluoride furnace tubes were fabricated by Adrian G. Allison, Group CMR-6.



  
the furnace after 15 hours use. Somewhat heavier nickel wire than is now being used would no doubt extend the life of the furnace. As an unfortunate consequence of the corrosion of the nickel wire furnace, it is not possible to equate the plutonium hexafluoride production to the fluorine consumption, which can be measured conveniently.

To date approximately 1g of plutonium hexafluoride has been prepared in this reactor, and it has been found that the synthesis may be carried out with much greater convenience in this reactor than in any previously used.

Before use in the experiments described below, the plutonium hexafluoride produced in the reactor was purified by a two step process. First, the plutonium hexafluoride was exposed to potassium fluoride which specifically removes hydrogen fluoride by double salt formation. Second, the plutonium hexafluoride was subjected to a fractional sublimation step which was accomplished by the following sequence of operations:

a. The entire sample was condensed into a 5 ml Fluorothene tube at dry ice temperature.

b. The temperature was raised to 0°, and after five minutes at this temperature the more volatile gas phase was rapidly pumped away. Little plutonium hexafluoride is lost if the pumping time is limited to a few seconds, since the vapor pressure of plutonium hexafluoride at 0° is less than 2 cm of mercury.

c. Operation b was repeated.

[REDACTED]

d. A portion of the remaining plutonium hexafluoride was allowed to sublime from this vessel into the storage vessel, the last 10% of plutonium hexafluoride along with the less volatile concentrate being retained in the Fluoroethene tube.

The purity of the resulting sample has not been positively established. Although the experimental results presented are reasonably precise, i.e., to within a few per cent, their accuracy remains subject to some question until the purity of the plutonium hexafluoride can be positively established.

Vapor Pressure of Plutonium Hexafluoride  
In The Region from 0° to 63°C

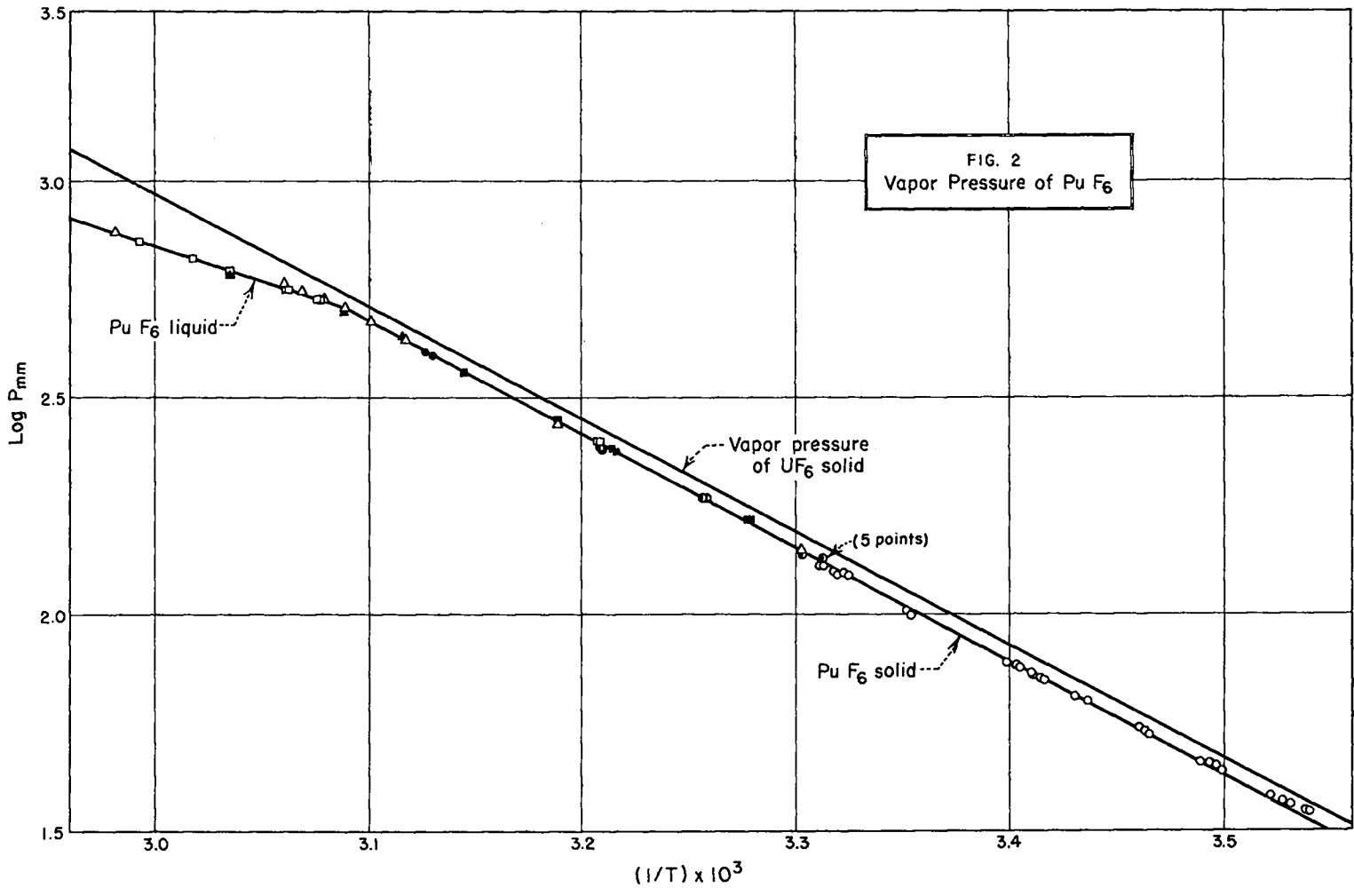
The vapor pressure measurements were made in a manner similar to that already described in LAMS 1118. The apparatus consisted of a Booth-Cromer(2) type gauge attached to a small copper U tube which contained the sample of plutonium hexafluoride. The gauge itself was controlled by a separate thermostat at a temperature about 5°C higher than the temperature of the sample to prevent the condensation of liquid or solid plutonium hexafluoride on the diaphragm. Despite this precaution some fouling of the diaphragm was evident after plutonium hexafluoride had been standing in the gauge for several days. This was undoubtedly due to deposition of a solid decomposition product of plutonium hexafluoride in the diaphragm chamber. Fortunately, only a small error in the measured pressure was introduced by this effect.

The pressure data obtained for various temperatures of plutonium



hexafluoride are shown as a plot of  $\log P_{\text{mm Hg}}$  (corrected to 0° and standard gravity) versus  $1/T_{\text{abs}}$  in Figure 2. The different shapes of points on the graph represent different samples of plutonium hexafluoride. For comparison, the same relation for uranium hexafluoride as given by I. Kirshenbaum(3) is also shown in Figure 2. It is seen that reasonably straight lines are obtained. This indicates that the purity of the sample is good. The slight curvature of the data toward pressures in excess of those predicted by a straight line function at temperatures below room temperature] may be a measure of lower heat of vaporization at low temperature, but some of the effect is thought to result from an experimental error.] The apparatus was arranged in such a way that it was not possible to cool the gauge much below room temperature even though the sample bath was at 0°; consequently, <sup>as already described</sup> a thermal gradient of some 25° existed between sample tube and gauge, and the temperature of the sample is subject to some question.

From Figure 2 it is seen that  $\log P$  of uranium hexafluoride minus  $\log P$  of plutonium hexafluoride is about 0.35 for each temperature in the solid-gas system. Also, for the same pressure of plutonium hexafluoride and uranium hexafluoride in the solid-gas system, the temperature of uranium hexafluoride is about 1.3° less than the temperature of plutonium hexafluoride. Plutonium hexafluoride, then is less volatile than uranium hexafluoride, but the difference is small.]



Sources of Error in the Vapor Pressure Measurements

The limits of error for the vapor pressure measurements are difficult to assess. [The average deviation of points from the line in Fig. 2 is 1.1% if data at temperatures below 15°C are excluded; however, this value, <sup>which is probably more due to</sup> for the precision of the results should not be regarded as a measure of accuracy.

The main sources of error are thought to be:

1. [Small amounts of impurities which might either raise or lower the pressure,
2. Faulty gauge action (due to deposition of solid decomposition products of plutonium hexafluoride in the diaphragm chamber of the gauge),
3. Failure to attain equilibrium between solid or liquid and gas phases of plutonium hexafluoride. <sup>This is the same as error may occur here</sup> This trouble was greater than would usually be encountered because of the continuous evolution of fluorine gas from plutonium hexafluoride and the fact that the sample and gauge were connected by a tubing of less than 1/16" internal diameter.
4. Improper correction of measured pressure for pressure due to fluorine gas.

Since a reliable figure cannot be given for the accuracy, no limit of error has been assigned to any of the results, although it is felt the results as given are probably correct to better than 2 or 3%.

Heat of Sublimation

From the slope of the line drawn for plutonium hexafluoride in

Figure 2, the heat of sublimation is calculated to be 12.1 Kcal. The value obtained from the uranium hexafluoride line is 11.89 Kcal.

### Triple Point

The intersection of solid and liquid lines shown in Figure 1 gives a triple point for plutonium hexafluoride at 50.7°C and 511mm Hg. The triple point for uranium hexafluoride occurs at 64.05°C and 1135mm Hg.(4)

An attempt to observe melting at the triple point visually by heating plutonium hexafluoride in a transparent Fluorothene tube was unsuccessful due to the corrosive attack by plutonium hexafluoride on Fluorothene in the neighborhood of the melting point of plutonium hexafluoride. Melting occurred over the range 48° to 50.3°C. The resulting liquid was a dark red-brown color.

### Heat of Vaporization

The value calculated from the slope of the liquid-vapor line in Figure 2 is 7.4 Kcal for the heat of vaporization of plutonium hexafluoride. From the data given by I. Kirshenbaum(3), the heat of vaporization of uranium hexafluoride can be extrapolated to the temperature range used in calculating the value for plutonium hexafluoride. The value for heat of vaporization of uranium hexafluoride obtained in this way is 7.15 Kcal.

### Heat and Entropy of Fusion

The difference between heat of sublimation and heat of vaporization gives 4.7 Kcal as the heat of fusion. The entropy of fusion is then 14.5 e.u.

For uranium hexafluoride, Kirshenbaum(3) gives 4.588 Kcal for heat of fusion and 13.61 e.v. for entropy of fusion.

#### Boiling Point

The boiling point of plutonium hexafluoride obtained from Figure 2 is 62.3°C. Uranium hexafluoride sublimes with a pressure of one atmosphere at 56.5°C.

#### Ice Point

The pressure of plutonium hexafluoride was measured as 17.3mm at 0°. (This value is outside the range of Figure 2.)

#### Trouton's Constant

Taking the values of boiling point and heat of vaporization of plutonium hexafluoride from Figure 2, Trouton's Constant is calculated to be 22.0.

#### Absorption Spectrum of Liquid Plutonium Hexafluoride

A Bausch & Lomb Spectrometer was used to measure the absorption spectrum of liquid plutonium hexafluoride. The sample was contained in the Fluorothene tube used for the attempt at measuring the triple point visually and the sample was, in fact, the same one used in that experiment. A tungsten lamp was placed behind the sample and the slit of the spectrometer was aligned in front of the sample. A masking screen was used so that only light which came through the sample was admitted to the slit of the spectrometer. During the measurements, the sample was kept at about 50°C by a stream of hot water directed on the Fluorothene tube.

The features of the absorption spectrum were as follows:


1. A prominent band at 560 to 565 millimicrons.
2. Weaker bands at 542 to 546 and 578 to 590 millimicrons.
3. Very faint line at 630 millimicrons. (So faint the observation is uncertain.)
4. Almost complete absorption below 525 millimicrons.
5. Darkness above 690. (This, however, is about the limit of vision.)

These features may be attributed to plutonium hexafluoride, because when the plutonium hexafluoride was pumped out of the tube all these features disappeared, except that darkness still prevailed above 690 millimicrons.

This measurement of the absorption spectrum, though crude, is being presented now, because it will be sometime before a more satisfactory experiment can be performed.

#### Purity of the Plutonium Hexafluoride

Although, as was noted previously, the purity of the plutonium hexafluoride used in these investigations has not been positively established, there is evidence that it was of reasonably high purity. The observation that the triple point temperature of a sample of unpurified plutonium hexafluoride was only 0.25°C lower than the triple point temperature of a fractionally sublimed sample indicates the sample was comparatively pure. At temperatures near the triple point, the vapor pressures of the unpurified plutonium hexafluoride were only



about 2% higher than the vapor pressures of the fractionally sublimed plutonium hexafluoride. The close agreement of the data with a straight line function when a plot was made of  $\log P$  against  $1/T$  is another indication of good purity of the sample. Finally, since the starting materials for the synthesis of plutonium hexafluoride were essentially pure plutonium tetrafluoride and fluorine of greater than 99% purity, it is difficult to account for the presence of impurities other than the decomposition products of plutonium hexafluoride. Even the presence of solid decomposition products did not appear to affect the vapor pressure of plutonium hexafluoride, since the pressure-temperature relationship observed for about 150 mg of plutonium hexafluoride when the pressure gauge was clean did not differ from that observed when, after several weeks of use, the gauge had become contaminated with an estimated 50 mg of solid decomposition product.

#### Radiodecomposition of Plutonium Hexafluoride

It has been observed previously that plutonium hexafluoride slowly decomposes to fluorine gas and a solid residue of yet undetermined composition. The rate of decomposition has been measured by observing the rate of pressure rise due to fluorine evolution when a known amount of plutonium hexafluoride decomposes in a known volume. The rate of decomposition of plutonium hexafluoride calculated from these data depends on the net reaction for the decomposition, and since the solid decomposition product has not yet been identified, the calculations have been made on the assumption that the net reaction is  $\text{PuF}_6 \rightarrow \text{PuF}_4 + \text{F}_2$ .

The decomposition rate has been found to be independent of temperature within experimental error over the range 0° to 50°C, and it has the constant value of 1.3% per day.

If it is assumed that the decomposition results from alpha radiation, the yield corresponds to 31.4 electron volts per molecule of plutonium hexafluoride decomposed. This calculation is based on the assumption that the alpha particle energy is 100% absorbed. It is assumed that alpha particles are emitted at the rate of  $1.4 \times 10^5$  per minute per microgram of plutonium and that the average energy is 5.1 mev. The result of the calculation is of the order of magnitude to be expected; although the uncertainty in the assumptions limits its accuracy considerably. However, the result of this calculation coupled with the temperature independence of the decomposition is strong evidence for the decomposition of plutonium hexafluoride by alpha radiation at moderate temperatures. These results indicate nothing with regard to thermodynamic stability; however, at temperatures up to 50°C it is believed that plutonium hexafluoride decomposes at the rate of 1.3% per day and that the decomposition results from the alpha activity of the plutonium.

#### Thermal Decomposition of Plutonium Hexafluoride

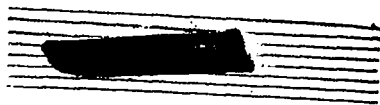
In an effort to learn something of the thermodynamic stability of plutonium hexafluoride at higher temperatures a 396.4 milligram sample contained in a 100 ml nickel cylinder was heated to a temperature of 580°C for 15 minutes. It was assumed there might be some decomposition





of plutonium hexafluoride to a non-volatile plutonium fluoride and free fluorine during the heating, and it was desired to find how much fluorine there would be in the equilibrium mixture. With the temperature held at 580°C, a valve was opened to permit removal of any volatile material from the hot tube.

The volatile material removed from the reactor was first passed through a trap maintained at the temperature of liquid nitrogen. This froze out any remaining plutonium hexafluoride and allowed fluorine to pass through. The contents of this trap were later transferred to a Fluorothene tube and it was seen that, at most, only a few per cent of the plutonium hexafluoride used in the experiment had survived the heating at 580°. The fluorine which passed through the first cold trap was then passed over calcium chloride where calcium fluoride was formed with the liberation of free chlorine. The chlorine was frozen out in a trap which contained frozen potassium iodide solution and which was cooled by liquid nitrogen. This trap was isolated by closing stopcocks, and the cold bath was removed so that the trap could warm to room temperature. As the frozen potassium iodide solution melted, the chlorine reacted with the potassium iodide to form potassium chloride and free iodine which immediately dissolved in the potassium iodide solution. The solution was titrated with sodium thiosulphate to determine the amount of iodine present. The analysis showed 1.247 millimoles of iodine. A previous test had shown the apparatus was only 86% efficient in determining a known quantity of fluorine; so if the




correction is applied, we may say the titration accounted for 1.45 milligramatoms of fluorine. This amount was obtained by the thermal decomposition of 1.12 millimoles of plutonium hexafluoride. Thus, more than one fluorine atom per molecule was given off by the plutonium hexafluoride. From the data given by Landau and Rosen(5) for the corrosion of nickel by fluorine at 500°C and 700°C, one would expect from 0.1 millimole to 1.75 millimole of fluorine to be consumed by the nickel apparatus under the conditions of this experiment. Thus it is seen that the difference between the fluorine found and that to be expected from the postulated decomposition of the sample of plutonium hexafluoride to plutonium tetrafluoride quite possibly could be accounted for by the corrosion of nickel.

It was found that the nickel cylinder used for the heating contained 360.4 mg. of residue at the conclusion of the experiment. If the 396.4 mg. of plutonium hexafluoride starting material had decomposed to plutonium tetrafluoride and fluorine during the heating, we would expect to find a plutonium tetrafluoride residue of 354 mg.

It may not be concluded from this, however, that the decomposition of plutonium hexafluoride at 580°C yields plutonium tetrafluoride and fluorine, at equilibrium, since we do not know what role the yet undiscovered plutonium pentafluoride and other possible intermediate fluorides may play in the equilibrium.

It can be concluded that plutonium hexafluoride at 580°C is very unstable and decomposes to fluorine gas and a non-volatile lower plutonium fluoride, and the amount of plutonium hexafluoride in the



equilibrium mixture does not exceed a few per cent of the original plutonium hexafluoride.

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