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THE HIGHER FLUORIDES OF PLUTONIUM

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The Higher Fluorides of Plutonium.

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In Volume 14B of Division IV of the National Nuclear Energy Series, Plutonium Project Record, Brewer, Bromley, Gilles, and Lofgren<sup>(1)</sup> have presented a systematic set of thermodynamic data for most of the known compounds of plutonium. From the data given by Fried and Davidson<sup>(2)</sup>, it is now possible to extend the tabulation of data for the compounds of plutonium to include  $\text{PuF}_4$ ,  $\text{PuF}_5$ , and  $\text{PuF}_6$ .

Thermodynamic data will be given for these compounds which are consistent with the data given for the other plutonium compounds by Brewer, Bromley, Gilles, and Lofgren<sup>(1)</sup> and with the published data which deal with the plutonium fluorides.

Determination of Thermodynamic Data

$\text{PuF}_4$  - The melting point, heat and entropy of fusion, vapor pressure, boiling points, and heat and entropy of vaporization were taken the same as the corresponding values for  $\text{UF}_4$  which are given by Brewer, Bromley, Gilles and Lofgren.<sup>(3)</sup> One might expect  $\text{PuF}_4$  to be slightly more volatile than  $\text{UF}_4$ , but the difference will not be enough to affect the calculations to be made here. Zachariassen<sup>(4)</sup> has reported that  $\text{PuF}_4$  forms light brown or cream pink monoclinic  $\text{ZrF}_4$  type crystals with a density of 7.0 g/cc. A heat of formation has not been measured but it is possible to make estimates of its value.

The first method which can be used is to consider the free energies of formation of the aqueous ions of uranium and plutonium. From the data on the aqueous ions of plutonium given by Brewer, Bromley, Gilles and Lofgren<sup>(1)</sup>, we find that the formal potential for  $\text{Pu}^{+3} \rightarrow \text{Pu}^{+4}$  in 1M HCl is 36.6 kcal. more positive than the value for the corresponding uranium potential<sup>(3)</sup>. By taking a 37 kcal. smaller difference between

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the heats of formation of  $\text{PuF}_4$  and  $\text{PuF}_3$  than between  $\text{UF}_4$  and  $\text{UF}_3$ , one obtains for the heat of formation of  $\text{PuF}_4$ ,  $\Delta H = -424$  kcal/mol.

The second method is to use the aqueous heat content values in the same manner. According to the value used in the uranium report<sup>(3)</sup> the difference between the heats of formation in 0.5 or 1M  $\text{HClO}_4$  for  $\text{U}^{+4}$  and  $\text{U}^{+3}$  is -23.7 kcal, while the corresponding Pu difference is +13 kcal. This also gives us a 37 kilocalorie smaller difference between  $\text{PuF}_4$  and  $\text{PuF}_3$  heats of formation than between  $\text{UF}_4$  and  $\text{UF}_3$ . Either of these procedures is equivalent to assuming identical free energies and heats of solution for corresponding uranium and plutonium compounds.

Another method of determining the heat of formation of  $\text{PuF}_4$  is based upon the observations of Fried and Davidson<sup>(2)</sup> who reported that the reaction  $4 \text{PuF}_3 + \text{O}_2 = 3 \text{PuF}_4 + \text{PuO}_2$  proceeds in an atmosphere of oxygen at  $873^\circ\text{K}$ . but that is reversed in a vacuum at the same temperature. These data are consistent with  $\Delta H_{298} = -375$  for  $\text{PuF}_3$  and  $\Delta H_{298} = -424$  kilocal for  $\text{PuF}_4$  if the equilibrium constant at  $873^\circ\text{K}$  is taken as 800 which is reasonable, but the data do not allow a precise fixing of the heats.  $\Delta H_{298} = -424 \pm 4$  kilocalories is accepted as the heat of formation of  $\text{PuF}_4$  which is most consistent with the available data.

Figure 1 indicates that  $\text{PuF}_4$  vaporizes with some  $\text{PuF}_5(\text{g})$  and  $\text{PuF}_3(\text{s})$  formed. As the temperature is raised,  $\text{PuF}_4(\text{g})$  is formed at the expense of these disproportionation products. As the temperature is raised further,  $\text{PuF}_4(\text{g})$  decomposes to  $\text{F}(\text{g})$  and  $\text{PuF}_3(\text{g})$  which itself at higher temperatures and lower pressures decomposes to monatomic gaseous elements. It should be pointed out that in view of uncertainties in the entropy and heat values, none of the equilibrium constants can be calculated closer than a factor of ten. But they do still give an indication of what probably are the important species under the specified condition.

**$\text{PuF}_5$**  Plutonium pentafluoride has not been prepared in a state in which it could be studied. It will probably have the tetragonal  $\beta\text{-UF}_5$  structures although a cubic

$\text{PuF}_{4.5}$  may also exist in addition to other analogues of the uranium system such as  $\text{U}_{3.13}\text{F}_{13}$ .<sup>(3)</sup> Values of the melting point, heat and entropy of fusion, vapor pressures, boiling point, and heat and entropy of vaporization are taken the same as for  $\beta\text{-UF}_5$  the high temperature form of  $\text{UF}_5$ . Estimates of  $\frac{\Delta F - \Delta H_{298}}{T}$  are likewise based upon the values for  $\beta\text{-UF}_5$ .<sup>(3)</sup>

The heat of formation can be estimated from a consideration of the aqueous potentials for the plutonium and uranium system and the heats of formation of uranium fluorides. The  $\text{Pu}^{+3} - \text{PuO}_2^+$  aqueous free energy difference is 49.5 kcal more positive than the corresponding  $\text{U}^{+3} - \text{UO}_2^+$  free energy<sup>(3)</sup> difference in 1M HCl.  $\beta$ -uranium pentafluoride<sup>(3)</sup> was found to have a heat of formation 128.5 kcal more negative than  $\text{UF}_3$ . Thus the heat of formation of  $\beta\text{-PuF}_5$  would be  $128.5 - 49.5 = 79$  kcal more negative than the heat of formation of  $\text{PuF}_3$ . This is equivalent to assuming heats, entropies, and free energies of solution identical for corresponding Pu and U compounds. This would give  $\Delta H = -454$  kcal/mol.

The heat of formation can be also estimated from dry chemistry observations. Fried and Davidson<sup>(2)</sup> have found that upon heating  $\text{PuF}_4$  in a vacuum  $\text{PuF}_3$  is produced. They have assumed that the reaction  $\text{PuF}_4 = \text{PuF}_3 + 1/2 \text{F}_2$  occurs at about  $1000^\circ\text{K}$ . However values for the heats and entropies of these compounds which would predict this reaction going would be very unreasonable in comparison with values for similar compounds and from our values we calculate that the fluorine pressure over solid  $\text{PuF}_3$  and  $\text{PuF}_4$  at  $1000^\circ\text{K}$  is about  $10^{-8.5}$  atm. which would not account for the formation of  $\text{PuF}_3$  at an appreciable rate from this reaction. We have believed that a more likely explanation of the formation of  $\text{PuF}_3$  is that the reaction  $2 \text{PuF}_4 = \text{PuF}_5(\text{g}) + \text{PuF}_3$  proceeds at elevated temperatures. By assuming that this reaction does occur we calculate from the work of Fried and Davidson<sup>(2)</sup> that the heat of formation of  $\text{PuF}_5$  should be between -448 and -460 kcal/mol.

Since the latter method is based upon very approximate estimates from qualitative results, it seems best to take  $\Delta H = -454 \pm 5$  kcal/mol for the heat of for-

ation of  $\text{PuF}_5(\text{s})$ . In the fluoride system this heat is probably the most uncertain relative to the others. In view of the rather large uncertainties in the heats of formation given for both  $\text{PuF}_4$  and  $\text{PuF}_5$ , calculations based on these heats are rather uncertain, but they should be useful in indicating the probable behavior and thus in indicating the best procedures for further study.

The calculated results indicate in the first place, that  $\text{PuF}_4$  does not decompose to  $\text{F}_2$  at temperatures in the neighborhood of  $1000^\circ\text{K}$ . The calculated pressure of fluorine over solid  $\text{PuF}_3$  and solid  $\text{PuF}_4$  at  $1000^\circ\text{K}$  is about  $10^{-17}$  atm.  $\text{F}_2$  and  $10^{-8.5}$  atm. monatomic  $\text{F}$ .

In the second place,  $\text{PuF}_4$  should be oxidized by an atmosphere of fluorine at all reasonable temperatures. Further,  $\text{PuF}_4$ , if heated, will disproportionate to  $\text{PuF}_3(\text{s})$  and to  $\text{PuF}_5(\text{g})$  at an appreciable pressure.

$\text{PuF}_4$  should be oxidized in an atmosphere of fluorine to  $\text{PuF}_6(\text{g})$  at temperatures even considerably above the normal boiling point of  $\text{PuF}_5$ .

Thermodynamically both copper and nickel (which are used by experimenters in experimental work on higher fluorides) should reduce all higher fluorides to  $\text{PuF}_3$ . The rate of this reaction is probably rather slow.

Disproportionation of  $\text{PuF}_5$  should produce at its own boiling point,  $1000^\circ\text{K}$ , appreciable quantities of  $\text{PuF}_6(\text{g})$ .

Pure  $\text{PuF}_5$  could be prepared by passing  $\text{PuF}_6(\text{g})$  over solid  $\text{PuF}_4$  which has been heated to a temperature at which the reaction will take place. The lowest possible temperature should be used since the reaction is exothermic. If  $\text{PuF}_5(\text{g})$  were to be evolved it could be condensed and subsequently could be purified from the  $\text{PuF}_6$  by fractional sublimation.

Probably the simplest method of preparing  $\text{PuF}_5$  is to heat  $\text{PuF}_4$  in a vacuum to about  $1000^\circ\text{K}$  and collect the  $\text{PuF}_5$  which vaporizes. At this temperature the partial pressure of  $\text{PuF}_5$  due to disproportionation is calculated to be about  $2 \times 10^{-5}$  atmospheres while the vapor pressure of  $\text{PuF}_4$  is about  $2 \times 10^{-6}$  atmos-

spheres. This method should give a fairly pure product and does not require elaborate preparation since especially pure  $\text{PuF}_4$  is not required and is readily obtainable.

Calculations based on the data in the tables indicate that as the temperature is raised,  $\text{PuF}_5(\text{g})$  decomposes successively into  $\text{PuF}_4(\text{g})$ ,  $\text{PuF}_3(\text{g})$ , and  $\text{Pu}(\text{g})$  and  $\text{F}(\text{g})$ .  $\text{PuF}_5(\text{g})$  is the main species in a system of overall composition  $\text{PuF}_5$  at one atmosphere total pressure to about 2500°K., while at  $10^{-3}$  atmospheres total pressure only to about 1800°K. and at  $10^{-6}$  atm. to about 1400°K.  $\text{PuF}_4(\text{g})$  is the main halide species above the previous temperatures quoted to about 3400-3800°K at one atm. total pressure, to about 2400-2600°K. at  $10^{-3}$  atm. and to about 1900°K. at  $10^{-6}$  atm.

$\text{PuF}_6$  The melting point, heat and entropy of fusion, vapor pressures, boiling points, heat and entropy of vaporization are taken the same as for  $\text{UF}_6$  while the values of  $\frac{\Delta F - \Delta H_{298}}{T}$  were estimated from corresponding values for  $\text{UF}_6$  as tabulated by the authors<sup>(3)</sup>. The heat of formation was obtained according to the first method discussed for  $\text{PuF}_4$ . Due to the smaller crystal radius to be expected for Pu compared to U, the heat was reduced one kilocalorie due to greater crowding of the F atoms.

Calculations based upon the data presented in the tables indicate that fluorine will oxidize  $\text{PuF}_5$  to  $\text{PuF}_6$  at temperatures usually encountered and thus one should obtain  $\text{PuF}_6$  rather than  $\text{PuF}_5$  in fluorine atmospheres. However,  $\text{PuF}_6$  should not be very stable and should be a strong oxidizing agent. As in the case of  $\text{PuF}_5$ , the results are obtained by thermodynamic calculations which, in themselves, are exact, but are based on estimated heats. In view of the large uncertainties in the estimated heats, the results of the calculations must be accepted with caution.

$\text{PuF}_6$  is a gas boiling slightly above room temperature and thus most of the important reactions will occur in the gaseous phase. It may probably be prepared by heating any lower fluoride in fluorine. The gas coming off  $\text{PuF}_4$  heated in

Fluorine could be passed through a series of traps at somewhat lower temperatures such that only the  $\text{PuF}_5$  present would be condensed out first; following that there would be condensation of  $\text{PuF}_6$  while the carrying gas would go on through.

Alternately the sublimates could all be condensed in a cold trap soon after they were vaporized and then purification could be accomplished by means of fractional distillation.

It must be emphasized that the very pure substances must be used to avoid contamination by oxygen and water resulting in the formation of oxyfluorides, which would probably be less volatile.

Brewer, Bronley, Gilles and Lofgren<sup>(1)</sup> have given figures showing the various species present in the gaseous phase when  $\text{PuF}_3$ ,  $\text{PuCl}_3$ ,  $\text{PuBr}_3$ , and  $\text{PuI}_3$  are heated. Figure 1 of this paper shows the composition of the gaseous phase when a sample of composition  $\text{PuF}_4$  is heated in a closed container at constant pressure. Figure 1 shows that as the temperature is raised,  $\text{PuF}_4$  concentration builds up, but not as one would expect if simple evaporation were the only process occurring.  $\text{PuF}_4(\text{s})$  disproportionates to a large extent to  $\text{PuF}_5(\text{g})$  and also solid  $\text{PuF}_3$ . This presence of another gaseous species in a system of fixed total pressure, of course limits the pressure of the main species. This reaction is endothermic and therefore, as the temperature is raised, goes to a greater extent. However, above the boiling point of  $\text{PuF}_4$ , the main reaction for disproportionation becomes  $2\text{PuF}_4(\text{g}) = \text{PuF}_5(\text{g}) + \text{PuF}_3$ . As this reaction is exothermic, it thus goes to a smaller extent as the temperature is raised. It can be seen therefore, that at the boiling point of  $\text{PuF}_4$ , the  $\text{PuF}_5$  will have its maximum concentration and that above this temperature its concentration will decrease. As the temperature is raised appreciably above the boiling point of  $\text{PuF}_4$ , the latter decomposes to  $\text{PuF}_3(\text{g})$  and  $\text{F}(\text{g})$ . At the temperatures at which this decomposition occurs both  $\text{PuF}_3(\text{s})$  or (l) and  $\text{F}_2$  are unstable. As the percentage of  $\text{PuF}_4$  decreases, the percentages of  $\text{PuF}_3$  and  $\text{F}$  rise together. At higher tempera-

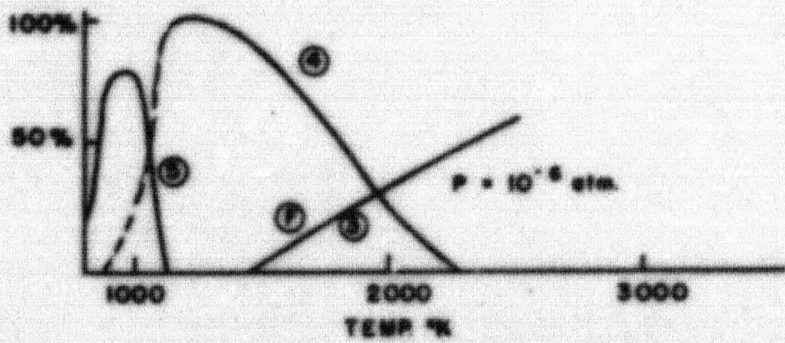
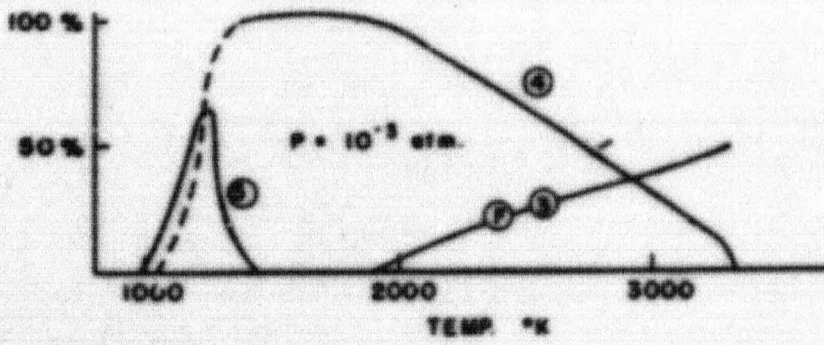
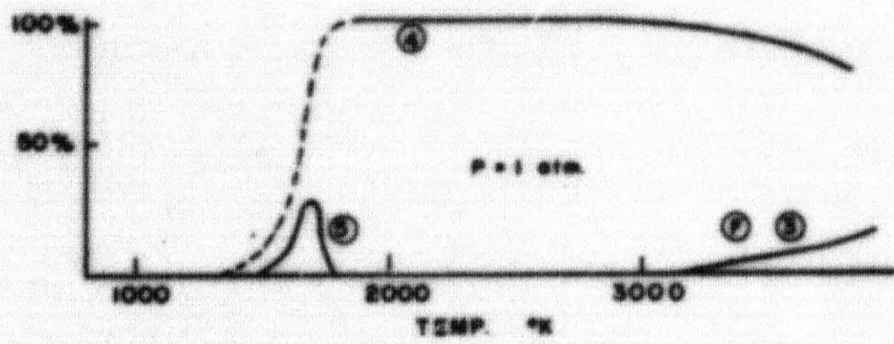


FIG. 1 GASEOUS EQUILIBRIUM  
OVERALL COMPOSITION,  $PuF_4$

Ms 75

- ① -  $PuF_4$
- ② -  $PuF_3$
- ③ -  $PuF$
- ④ - MONATOMIC FLUORINE



tures  $\text{PuF}_3$  becomes unstable, decomposing to the monatomic gaseous elements. The final percentages of  $\text{Pu(g)}$  and  $\text{F(g)}$  are 20% and 80% corresponding to the composition  $\text{PuF}_4$ .

It should be noted here that probably at high temperatures appreciable concentrations of lower fluorides, e.g.  $\text{PuF}$  and  $\text{PuF}_2$ , exist in the gaseous equilibrium. These are ignored in these calculations and graphs since there are absolutely no data on them.

Beyond giving one an idea of the chemistry of the individual compounds at high temperatures, these graphs have a very important function. One can tell by a glance at the graphs what species are important and which therefore, should be used in all calculations under those conditions. For example, if one were to consider a reaction involving the oxidation of a metal by plutonium tetrafluoride in the temperature region  $2000^\circ\text{-}2500^\circ\text{K}$  at a total pressure of  $10^{-6}$  atm., one would obtain a grossly incorrect conclusion if he were to base his calculations on the equation  $\text{PuF}_4 + \text{M}$  whereas a reasonably good value could be obtained if he used the equation  $\text{PuF}_3 + \text{M}$ . In all thermodynamic considerations it is essential that the species which are being considered are the ones which actually exist in the system. The graphs are useful for this purpose and can save much time and trouble considering all the various possible decompositions and disproportionations which can occur in a system.

It should be emphasized that these figures are only qualitative and that the heats and free energies of Table I should be used to calculate more nearly exact equilibria when once the species have been determined from the graphs.

To summarize the thermodynamic data for the halides of plutonium, a portion of Table 3 from paper 6.40 by Brewer, Bromley, Gilles and Lofgren<sup>(1)</sup> is given here together with the data for  $\text{PuF}_4$ ,  $\text{PuF}_5$ , and  $\text{PuF}_6$ . Some of the data given in paper 6.40 have been corrected to agree with the most recent values given by Westrum and Eyring<sup>(5)</sup>, Westrum and Robinson<sup>(6)</sup>, and Westrum<sup>(7)</sup>.

Table I

Values of the Free-Energy Function  $(\Delta F - \Delta H_{298})/T$  and  $\Delta H_{298}$ 

Compound	$(\Delta F - \Delta H_{298})/T$ Calories per °K.				$\Delta H_{298}$ kcal*
	298°K	500°K	1000°K	1500°K	
$\text{PuF}_3$	60	59	59	58	-375 ± 1
$\text{PuF}_4$	74	74	70	66(1)	-424 ± 4
$\beta\text{-PuF}_5$	89	88	84(1)		-454 ± 5
$\text{PuF}_6(\text{g})$	68(g)	67(g)	65(g)		-453 ± 5(g)
$\text{PuCl}_3$	54	54	53	50(1)	-230.0
$\text{PuCl}_4$	72	72	68(1)		-230.
$\text{PuBr}_3$	52	52	50(1)	48(1)	-198.8
$\text{PuI}_3$	52	52	49	48(1)	-155.
$\text{PuO}_2$	43	42	41	41	-251.

\*All values are based upon gaseous standard states for fluorine, chlorine, bromine, iodine, oxygen, and solid plutonium.

### Summary

The data published in the National Nuclear Energy Series, Plutonium Project Record, Division IV, Vol. 14B have been used to complete the tabulation of the thermodynamic properties of the compounds of plutonium. From these data, it can be shown that  $\text{PuF}_5$  is a stable compound in both condensed and gaseous phases. Methods of preparation are indicated. The data indicate that  $\text{PuF}_6$  should be of some importance in the gaseous phase, but it should be an extremely powerful oxidizing agent and thus should be difficult to prepare. Methods of preparation are suggested.

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