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Authors
Brewer, Leo
Bromley, Leroy
Gilles, Paulo
et al.

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Leo Brewer, LeRoy A. Bromley,

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The Higher Fluorides of Plutonium.

Leo Brewer, LeRoy A. Bromley, Paul W. Gilles* and Norman L. Lofgren**

In Volume 14B of Division IV of the National Nuclear Energy Series, Plutonium Project Record, Brewer, Bromley, Gilles, and Lofgren[1] have presented a systematic set of thermodynamic data for most of the known compounds of plutonium. From the data given by Fried and Davidson[2], it is now possible to extend the tabulation of data for the compounds of plutonium to include PuF_4, PuF_5, and 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[1] and with the published data which deal with the plutonium fluorides.

Determination of Thermodynamic Data

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 UF_4 which are given by Brewer, Bromley, Gilles and Lofgren.[3] One might expect PuF_4 to be slightly more volatile than UF_4, but the difference will not be enough to affect the calculations to be made here. Zachariasen[4] has reported that PuF_4 forms light brown or cream pink monoclinic 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[1], we find that the formal potential for Pu^{+3}--Pu^{+4} in 1M HCl is 36.6 kcals. more positive than the value for the corresponding uranium potential[3]. By taking a 37 kcal. smaller difference between

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*Present address, University of Kansas, Lawrence, Kansas.
**Present address, Chico State College, Chico, California.

the heats of formation of PuF_4 and PuF_3 than between UF_4 and UF_3, one obtains for the heat of formation of PuF_4, $\Delta H = -424$ kcals/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[3] the difference between the heats of formation in 0.5 or 1M $HClO_4$ for U^{+4} and U^{+3} is -23.7 kcals, while the corresponding Pu difference is +13 kcals. This also gives us a 37 kilocalorie smaller difference between PuF_4 and PuF_3 heats of formation than between UF_4 and 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 PuF_4 is based upon the observations of Fried and Davidson[2] who reported that the reaction $4\ PuF_3 + O_2 = 3\ PuF_4 + PuO_2$ proceeds in an atmosphere of oxygen at 873°K. but that is reversed in a vacuum at the same temperature. These data are consistent with $\Delta H_{298} = -375$ for PuF_3 and $\Delta H_{298} = -424$ kilocals for PuF_4 if the equilibrium constant at 873°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 PuF_4 which is most consistent with the available data.

Figure 1 indicates that PuF_4 vaporizes with some $PuF_5(g)$ and $PuF_3(s)$ formed. As the temperature is raised, $PuF_4(g)$ is formed at the expense of these disproportionation products. As the temperature is raised further, $PuF_4(g)$ decomposes to $F(g)$ and $PuF_3(g)$ 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.

$\underline{PuF_5}$ Plutonium pentafluoride has not been prepared in a state in which it could be studied. It will probably have the tetragonal β-UF_5 structures although a cubic

$PuF_{4.5}$ may also exist in addition to other analogues of the uranium system such as U_3F_{13}.[3] 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 β-UF_5 the high temperature form of UF_5. Estimates of $\dfrac{\Delta F - \Delta H_{298}}{T}$ are likewise based upon the values for β-UF_5.[3]

The heat of formation can be estimated from a consderation of the aqueous potentials for the plutonium and uranium system and the heats of formation of uranium fluorides. The Pu^{+3} - PuO_2^+ aqueous free energy difference is 49.5 kcals more positive than the corresponding U^{+3}-UO_2^+ free energy[3] difference in 1M HCl. β-uranium pentafluoride[3] was found to have a heat of formation 128.5 kcals more negative than UF_3. Thus the heat of formation of β-PuF_5 would be 128.5-49.5 = 79 kcals more negative than the heat of formation of PuF_3. This is equivalent to assuming heats, entropies, and free energies of solution identical for corresponding Pu and U compounds. This would give ΔH = -454 kcals/mol.

The heat of formation can be also estimated from dry chemistry observations. Fried and Davidson[2] have found that upon heating PuF_4 in a vacuum PuF_3 is produced. They have assumed that the reaction PuF_4 = PuF_3 + 1/2 F_2 occurs at about 1000°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 PuF_3 and PuF_4 at 1000°K is about $10^{-8.5}$ atm. which would not account for the formation of PuF_3 at an appreciable rate from this reaction. We have believed that a more likely explanation of the formation of PuF_3 is that the reaction 2 PuF_4 = PuF_5(g) + PuF_3 proceeds at elevated temperatures. By assuming that this reaction does occur we calculate from the work of Fried and Davidson[2] that the heat of formation of PuF_5 should be between -448 and -460 kcals/mol.

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

mation of $PuF_5(s)$. 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 PuF_4 and 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 PuF_4 does not decompose to F_2 at temperatures in the neighborhood of 1000°K. The calculated pressure of fluorine over solid PuF_3 and solid PuF_4 at 1000°K is about 10^{-17} atm. F_2 and $10^{-8.5}$ atm. monatomic F.

In the second place, PuF_4 should be oxidized by an atmosphere of fluorine at all reasonable temperatures. Further, PuF_4, if heated, will disproportionate to $PuF_3(s)$ and to $PuF_5(g)$ at an appreciable pressure.

PuF_5 should be oxidized in an atmosphere of fluorine to $PuF_6(g)$ at temperatures even considerably above the normal boiling point of PuF_5.

Thermodynamically both copper and nickel (which are used by experimenters in experimental work on higher fluorides) should reduce all higher fluorides to PuF_3. The rate of this reaction is probably rather slow.

Disproportionation of PuF_5 should produce at its own boiling point, 1000°K, appreciable quantities of $PuF_6(g)$.

Pure PuF_5 could be prepared by passing $PuF_6(g)$ over solid 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 $PuF_5(g)$ were to be evolved it could be condensed and subsequently could be purified from the PuF_6 by fractional sublimation.

Probably the simplest method of preparing PuF_5 is to heat PuF_4 in a vacuum to about 1000°K and collect the PuF_5 which vaporizes. At this temperature the partial pressure of PuF_5 due to disproportionation is calculated to be about 2×10^{-5} atmospheres while the vapor pressure of PuF_4 is about 2×10^{-6} atmos-

pheres. This method should give a fairly pure product and does not require elaborate preparation since especially pure PuF_4 is not required and is readily obtainable.

Calculations based on the data in the tables indicate that as the temperature is raised, $PuF_5(g)$ decomposes successively into $PuF_4(g)$, $PuF_3(g)$, and $Pu(g)$ and $F(g)$. $PuF_5(g)$ is the main species in a system of overall composition 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. $PuF_4(g)$ 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.

$\underline{PuF_6}$ The melting point, heat and entropy of fusion, vapor pressures, boiling points, heat and entropy of vaporization are taken the same as for UF_6 while the values of $\dfrac{\Delta F - \Delta H_{298}}{T}$ were estimated from corresponding values for UF_6 as tabulated by the authors[3]. The heat of formation was obtained according to the first method discussed for 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 PuF_5 to PuF_6 at temperatures usually encountered and thus one should obtain PuF_6 rather than PuF_5 in fluorine atmospheres. However, PuF_6 should not be very stable and should be a strong oxidizing agent. As in the case of 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.

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 PuF_4 heated in

fluorine could be passed through a series of traps at somewhat lower temperatures such that only the PuF_5 present would be condensed out first; following that there would be condensation of 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, Bromley, Gilles and Lofgren[1] have given figures showing the various species present in the gaseous phase when PuF_3, $PuCl_3$, $PuBr_3$, and PuI_3 are heated. Figure 1 of this paper shows the composition of the gaseous phase when a sample of composition PuF_4 is heated in a closed container at constant pressure. Figure 1 shows that as the temperature is raised, PuF_4 concentration builds up, but not as one would expect if simple evaporation were the only process occuring. $PuF_4(s)$ disproportionates to a large extent to $PuF_5(g)$ and also solid 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 PuF_4, the main reaction for disproportionation becomes $2PuF_4(g) = PuF_5(g) + PuF_3$. 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 PuF_4, the 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 PuF_4, the latter decomposes to $PuF_3(g)$ and $F(g)$. At the temperatures at which this decomposition occurs both $PuF_3(s)$ or (l) and F_2 are unstable. As the percentage of PuF_4 decreases, the percentages of PuF_3 and F rise together. At higher tempera-
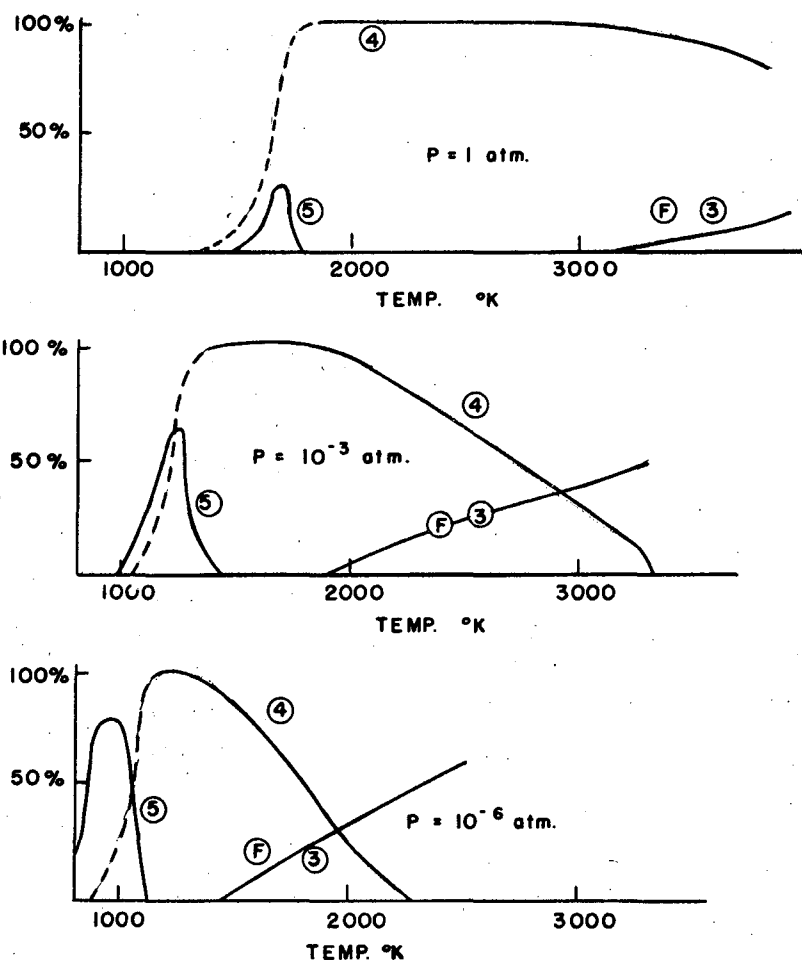
FIG. I GASEOUS EQUILIBRIUM
OVERALL COMPOSITION, PuF₄

③ - PuF₃   ⑤ - PuF₅

④ - PuF   Ⓕ - MONATOMIC FLUORINE

Mu 75

tures PuF_3 becomes unstable, decomposing to the monatomic gaseous elements. The final percentages of $Pu(g)$ and $F(g)$ are 20% and 80% corresponding to the composition PuF_4.

It should be noted here that probably at high temperatures appreciable concentrations of lower fluorides, e.g. PuF and 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 tetra-fluoride in the temperature region 2000°-2500°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 $PuF_4 + M$ whereas a reasonably good value could be obtained if he used the equation $PuF_3 + M$. 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 disproportions 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[1] is given here together with the data for PuF_4, PuF_5, and 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[5], Westrum and Robinson[6], and Westrum[7].

Table I

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

Com-pound	$(\Delta F - \Delta H_{298})/T$ Calories per °K.				ΔH_{298},* kcal
	298°K	500°K	1000°K	1500°K	
PuF$_3$	60	59	59	58	-375 $\pm$ 1
PuF$_4$	74	74	70	66(1)	-424 $\pm$ 4
β-PuF$_5$	89	88	84(1)		-454 $\pm$ 5
PuF$_6$(g)	68(g)	67(g)	65(g)		-453 $\pm$ 5(g)
PuCl$_3$	54	54	53	50(1)	-230.0
PuCl$_4$	72	72	68(1)		-230.
PuBr$_3$	52	52	50(1)	48(1)	-198.8
PuI$_3$	52	52	49	48(1)	-155.
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 PuF_5 is a stable compound in both condensed and gaseous phases. Methods of preparation are indicated. The data indicate that 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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