Mass Spectrometric Studies of Plutonium Compounds at High Temperatures. II. The Enthalpy of Sublimation of Plutonium(III) Fluoride and the Dissociation Energy of Plutonium(I) Fluoride[1]

R. A. Kent

Contribution from the Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87544. Received April 26, 1968

Abstract: A mass spectrometric investigation of the sublimation of PuF_3 in the temperature range 1243–1475°K has established the principal vapor species to be $PuF_3(g)$. The vapor pressure is given by the equation $\log P$ (atm) = $[(-20,734 \pm 118)/T°K] + (9.288 \pm 0.087)$. The enthalpy and entropy of sublimation at 298°K are calculated to be 101 ± 3 kcal mole^{-1} and 51.6 ± 2.5 eu, respectively. Studies of the equilibria among gaseous species over the mixture Pu + PuF_3 yielded the atomization energies of $PuF_3(g)$ and $PuF_2(g)$ and the dissociation energy of $PuF(g)$.

The vapor pressure of PuF_3 has been measured by Phipps, *et al.*,[2] who employed a tantalum Knudsen cell and a target collection technique. Over the range 1220–1440°K, they obtained the second-law enthalpy $\Delta H_{1310} = 96.6$ kcal mole^{-1}. Over the range 1440–1661°K they obtained $\Delta H_{1545} = 88.8$ kcal mole^{-1}. The difference in the two enthalpy values was attributed to sample melting at 1440°K.

Westrum and Wallman,[3a] however, have shown that PuF_3 melts at 1699 ± 2°K. Thus the change in slope obtained by Phipps and coworkers at 1440°K cannot be due to melting. Westrum[3a] and Rand[3b] have both calculated a "best line" through all of the data of Phipps and coworkers and obtained a second-law enthalpy of vaporization of approximately 93 kcal mole^{-1} at 1400°K.

Carniglia and Cunningham[4] also employed a tantalum Knudsen cell and a target collection apparatus to measure the vapor pressure of PuF_3 over the range 1214–1444°K. They obtained a second-law enthalpy of sublimation of $\Delta H_{1347} = 103$ kcal mole^{-1}. Although the enthalpy values obtained by Phipps, *et al.*, and by Carniglia and Cunningham are in poor agreement, the PuF_3 vapor pressure values obtained in the two studies are in fairly good agreement in the range 1300–1400°K.

In this study, the vapor pressure and the enthalpy of sublimation of PuF_3 have been determined over the range 1243–1475°K employing the Knudsen technique and a mass spectrometer. In addition, gaseous equilibria involving $PuF_2(g)$ and $PuF(g)$ have been studied to determine the stabilities of these molecules.

Experimental Section

The mass spectrometer-Knudsen cell assembly has been described previously.[5] The PuF_3 powder used in this work was prepared by Dr. L. J. Mullins of this group, by treating plutonium peroxide with

HF(g) and $H_2(g)$ at 700°. X-Ray powder diffraction analyses indicated the resultant material to be single-phase PuF_3. Chemical analyses indicated the sample to consist of 80.57 wt % Pu and 19.10 wt % F (theoretical PuF_3: 80.74 wt % Pu, 19.26 wt % F). The major impurities were 400 ppm Am and 80 ppm Fe.

Results

A. Sublimation of PuF_3. The sublimation of PuF_3 was studied in the mass spectrometer over the temperature range 1243–1475°K. The only ionic species found to be due to molecules effusing from the tantalum Knudsen cell were PuF_2^+, PuF^+, Pu^+, and lesser amounts of PuF_3^+. The appearance potentials evaluated by the vanishing-current method, using background oxygen to calibrate the ionizing-electron voltage scale, were found to be 12.6 ± 0.5, 18.0 ± 1.0, and 25.0 ± 1.0 eV for PuF_2^+, PuF^+, and Pu^+, respectively. The PuF_3^+ signed was too low to enable one to measure its appearance potential. These values, together with the shapes of the ionization efficiency curves, indicate that these ions are formed by dissociative ionization of $PuF_3(g)$. Thus one concludes that the only vapor species above solid PuF_3 is $PuF_3(g)$. This vaporization process has been reported for other trifluorides, such as ScF_3,[6] YF_3,[6] LaF_3,[6] NdF_3,[7] CrF_3,[8] and MnF_3.[8]

The enthalpy of sublimation of PuF_3 was determined from measurements of the temperature dependence of the PuF_2^+ ion at 24 eV. By making use of the ion current–pressure relationship $P = KI^+T$[9] and the integrated form of the Clausius–Clapeyron equation, a value of ΔH_T, which is independent of the proportionality constant K, may be found from the slope of the curve obtained by graphing $\log (I^+T)$ *vs.* $1/T$. The slope of this curve yielded an enthalpy of sublimation of $\Delta H_{1365} = 94.9 \pm 0.5$ kcal mole^{-1}, where the uncertainty quoted is generated by the least-squares program.

In order to determine absolute pressures from the measured ion current data, the constant K was determined in the following manner. A weighed sample of previously degassed PuF_3 was vaporized from a tan-

(1) This work was sponsored by the U. S. Atomic Energy Commission.

(2) T. E. Phipps, G. W. Sears, R. L. Seiffert, and O. C. Simpson, *J. Chem. Phys.*, **18**, 713 (1950).

(3) (a) E. F. Westrum, Jr., and J. C. Wallman, *J. Am. Chem. Soc.*, **73**, 3530 (1951); (b) M. H. Rand, "Thermochemical Properties," in "Atomic Energy Review," Vol. 4, Special Issue No. 1, IAEA, Vienna, 1966.

(4) S. C. Carniglia and B. B. Cunningham, *J. Am. Chem. Soc.*, **77** 1451 (1955).

(5) R. A. Kent and J. A. Leary, Los Alamos Scientific Laboratory Report LA-3902, 1968.

(6) R. A. Kent, K. F. Zmbov, A. S. Kana'an, G. Besenbruch, J. D. McDonald, and J. L. Margrave, *J. Inorg. Nucl. Chem.*, **28**, 1419 (1966).

(7) K. F. Zmbov and J. L. Margrave, *J. Chem. Phys.*, **45**, 3167 (1966).

(8) K. F. Zmbov and J. L. Margrave, *J. Inorg. Nucl. Chem.*, **29**, 673 (1967).

(9) W. A. Chupka and M. G. Inghram, *J. Chem. Phys.*, **21**, 371 (1953).
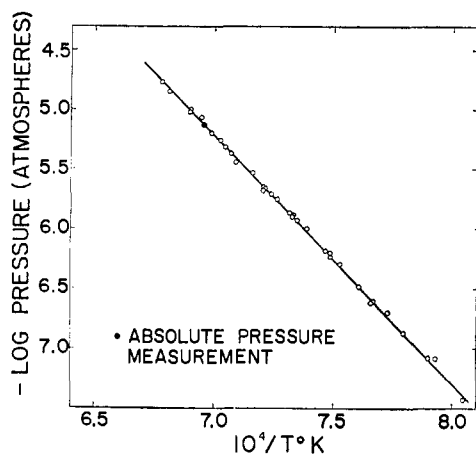
Figure 1. Vapor pressure data for PuF₃.

the data are presented in the order taken. These data yield the least-squares equation

$$\log P \text{ (atm)} = (9.288 \pm 0.087) - \frac{20{,}734 \pm 118}{T°K}$$

and are graphed in Figure 1. The second-law entropy of sublimation from the Clausius–Clapeyron plot is $\Delta S_{1365} = 42.5 \pm 0.4$ eu, where again the uncertainty quoted is that generated by the least-squares program.

Unfortunately no reliable heat capacity data exist for solid or gaseous PuF_3. The second-law enthalpy and entropy values were corrected to 298°K by assuming $\Delta C_p = -6$ cal mole^{-1} deg^{-1} for the sublimation process. Thus one obtains $\Delta H°_{298, \text{subl}} = 101 \pm 3$ kcal mole^{-1} and $\Delta S°_{298, \text{subl}} = 51.6 \pm 2.5$ eu, where the quoted uncertainties take into account possible errors in temperature measurement, the orifice area, and the ΔC_p value employed.

B. Stabilities of Plutonium Tri-, Di-, and Mono-fluorides. When the enthalpy of sublimation of PuF_3 is combined with the standard enthalpy of formation of $PuF_3(s)$, -371 ± 3 kcal mole^{-1},[3] the sublimation enthalpy of plutonium, 83.0 ± 0.5 kcal mole^{-1},[5] and the dissociation energy of $F_2(g)$,[11] one calculates the atomization energy of $PuF_3(g)$ to be $\Delta H_{298, \text{atom}} = 410 \pm 5$ kcal mole^{-1}. From this, one calculates the average bond energy, $\frac{1}{3}\Delta H_{\text{atom}}$, to be 137 ± 6 kcal mole^{-1} for $PuF_3(g)$.

When electrorefined plutonium metal[12] was added to the PuF_3 in the tantalum Knudsen cell and the mixture heated, the only ionic species due to molecules effusing from the cell were PuF_2^+, PuF^+, Pu^+, and small amounts of PuF_3^+. Again, the PuF_3^+ signal was too small to allow one to measure its appearance potential. The appearance potential values and the shapes of the ionization efficiency curves for the other ionic species indicated the presence in the vapor of $Pu(g)$, $PuF(g)$, and $PuF_2(g)$ in addition to $PuF_3(g)$. The appearance potential data are presented in Table II.

talum cell at a constant temperature, and the intensity of the PuF_2^+ peak was monitored as a function of time. At 1438°K, 2.93×10^{-2} g of PuF_3 effused in 180 min through an orifice of area 18.24×10^{-3} cm² and clausing factor 0.9958. By means of the well-known Knudsen equation,[10] one obtains $P = 7.41 \times 10^{-6}$ atm and $K = 8.75 \times 10^{-14}$ atm A^{-1} °K^{-1}. This value of K was combined with the experimentally determined values of (I^+T) to calculate the absolute pressure values of each temperature, as given in Table I, where

Table I. Vapor Pressure Data for PuF₃

Point	Temp, °K	Pressure, atm ($\times 10^6$)	$\Delta F°_T$, kcal mole^{-1}
A1[a]	1386	2.19	35.90
A2	1387	2.26	35.84
A3	1382	1.96	36.10
A4	1364	1.30	36.74
A5	1361	1.18	36.93
A6	1354	1.01	36.15
A7	1339	0.656	37.88
A8	1336	0.572	38.17
A9	1329	0.497	38.34
A10	1305	0.245	39.48
B1	1266	0.0830	41.02
B2	1294	0.199	39.67
B3	1336	0.631	37.61
B4	1367	1.36	36.69
B5	1414	4.24	34.76
B6	1449	9.53	33.29
B7	1423	5.47	34.27
B8	1377	1.79	36.22
C1	1261	0.0817	40.90
C2	1396	2.91	35.36
C3	1450	9.89	33.21
C4	1475	17.1	32.17
C5	1468	14.2	32.56
C6	1440	8.53	33.40
C7	1431	6.34	34.04
C8	1419	4.75	34.56
C9	1410	3.55	35.16
C10	1388	2.11	36.05
C11	1365	1.25	36.87
C12	1315	0.334	38.97
C13	1306	0.240	39.56
C14	1283	0.134	40.35
C15	1243	0.0370	42.27

[a] Runs A and B normalized to run C to account for changes in the gain of the electron multiplier.

Table II. Appearance Potentials and Neutral Precursors of Ions Observed above the Pu + PuF₃ System

Ion	Appearance potential, eV	Neutral precursor
Pu$^+$	5.2 ± 0.5	Pu
PuF$^+$	5.9 ± 0.5	PuF
	17.8 ± 0.5	PuF₃
PuF₂$^+$	6.4 ± 0.5	PuF₂
	13.0 ± 0.5	PuF₃

The intensities of the Pu^+, PuF^+, and PuF_2^+ ions were measured at various temperatures using low-energy electrons with energies 3–5 eV above thresholds. The portion of the PuF_2^+ ion current due to $PuF_3(g)$ was obtained from measurement at 24 eV by correcting for PuF_2^+ ions due to $PuF_2(g)$ assuming a linear increase of the intensity with the ionizing voltage. The ion current data were then used to calculate the ion current analogs

(10) J. L. Margrave in "Physico-Chemical Measurements of High Temperatures," J. Bockris, J. White, and J. MacKenzie, Ed., Butterworth & Co., Ltd., London, 1959.

(11) "JANAF Thermochemical Tables," The Dow Chemical Co., Midland, Mich., 1965.
(12) J. A. Leary and L. J. Mullins, Los Alamos Scientific Laboratory Report LA-3356-MS, 1965.

Table III. Heats of Sublimation and Bond Energies at 298°K

System	$-\Delta H_f°(\mathrm{MF_3(s)})$, kcal mole^{-1}	$\Delta H_{\mathrm{sub}}(\mathrm{MF_3(s)})$, kcal mole^{-1}	$\Delta H_{\mathrm{atom}}(\mathrm{MF_3(g)})$, kcal mole^{-1}	Av bond energy $^1/_3\Delta H_{\mathrm{atom}}$, kcal mole^{-1}	$D°_{298}(\mathrm{MF})$,[a] eV	Ref
Sc–F	380 ± 10	101 ± 5	438 ± 6	146 ± 6	6.11 ± 0.14	6[b]
Y–F	410.8 ± 0.8	115 ± 5	453 ± 6	151 ± 2	6.23 ± 0.22	6[b]
La–F	434 ± 10	108 ± 5	485 ± 15	162 ± 6	(6.53 ± 0.30)	6
Ce–F	429 ± 10	99 ± 3	482 ± 15	161 ± 5	(6.49 ± 0.30)	6
Nd–F	399 ± 10	94 ± 4	437 ± 10	146 ± 3	5.64 ± 0.13	7
Sm–F	425 ± 10	107 ± 1	424 ± 5	141 ± 5	5.51 ± 0.17	c
Eu–F	411 ± 10	101 ± 1	408 ± 5	136 ± 5	5.46 ± 0.17	c
Gd–F	406.5 ± 0.3	96 ± 5	443 ± 10	148 ± 5	6.42 ± 0.17	c
Dy–F	407 ± 15	117 ± 5	412 ± 10	137 ± 6	5.46 ± 0.17	d
Ho–F	405.8 ± 0.6	116 ± 2	410 ± 10	137 ± 6	5.33 ± 0.13	d
Er–F	402 ± 10	119 ± 5	422 ± 10	141 ± 6	5.90 ± 0.17	d
Pu–F	371 ± 3	101 ± 3	410 ± 5	137 ± 6	5.53 ± 0.30	This work

[a] Values in parentheses were estimated from the ratio for $D°_{298}/\Delta H_{\mathrm{atom}}$ obtained in the mass spectrometric investigations of the Nd, Sm, Eu, Gd, Dy, Ho, Er, and Pu fluoride systems. [b] K. F. Zmbov and J. L. Margrave, *J. Chem. Phys.*, **47**, 3122 (1967). [c] K. F. Zmbov and J. L. Margrave, *J. Inorg. Nucl. Chem.*, **29**, 59 (1967). [d] K. F. Zmbov and J. L. Margrave, *J. Phys. Chem.*, **70**, 3379 (1966).
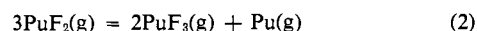
of the equilibrium constants for the following reactions

$$3\mathrm{PuF(g)} = \mathrm{PuF_3(g)} + 2\mathrm{Pu(g)} \qquad (1)$$
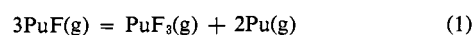
where K is given by

$$K = (I_{\mathrm{PuF_3}}{}^+)(I_{\mathrm{Pu}}{}^+)^2/(I_{\mathrm{PuF}}{}^+)^3$$

and

$$3\mathrm{PuF_2(g)} = 2\mathrm{PuF_3(g)} + \mathrm{Pu(g)} \qquad (2)$$

where

$$K = (I_{\mathrm{PuF_3}}{}^+)^2(I_{\mathrm{Pu}}{}^+)/(I_{\mathrm{PuF_2}}{}^+)^3$$

Plots of log K vs. $1/T$ for reactions 1 and 2 are shown in Figure 2. The enthalpies obtained are $\Delta H_{1414} = -23.4 \pm 4.6$ kcal mole^{-1} for reaction 1 and $\Delta H_{1417} = -28.7 \pm 2.4$ kcal mole^{-1} for reaction 2. Published C_p values for Pu(g)[13] and estimated C_p values for PuF(g), PuF$_2$(g), and PuF$_3$(g) were employed to correct the enthalpy values to 298°K. The values then become $\Delta H°_{298} = -29.6 \pm 5$ kcal mole^{-1} and $\Delta H°_{298} = -32.6 \pm 3$ kcal mole^{-1} for reactions 1 and 2, respectively.

When the enthalpy for reaction 1 is combined with the atomization energy of PuF$_3$(g), one calculates the dissociation energy of PuF(g) to be $D°_{298} = 127.5 \pm 7$ kcal mole^{-1}.

When the atomization energy of PuF$_3$(g) is combined with the dissociation energy of PuF(g) and the enthalpy of reaction 2, one obtains $\Delta H°_{298} = 135 \pm 8$ for the reaction

$$\mathrm{PuF_2(g)} = \mathrm{PuF(g)} + \mathrm{F(g)} \qquad (3)$$
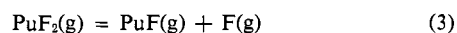
(13) R. C. Feber and C. C. Herrick, Los Alamos Scientific Laboratory Report LA-3184, 1965.

In summary, the respective energies (kcal mole^{-1}) for dissociating plutonium tri-, di-, and monofluorides are $D(\mathrm{F_2Pu-F}) = 147 \pm 10$, $D(\mathrm{FPu-F}) = 135 \pm 8$, $D(\mathrm{Pu-F}) = 128.7 \pm 7$, while the average bond energy in PuF$_3$(g) is 137 ± 6 kcal mole^{-1}.
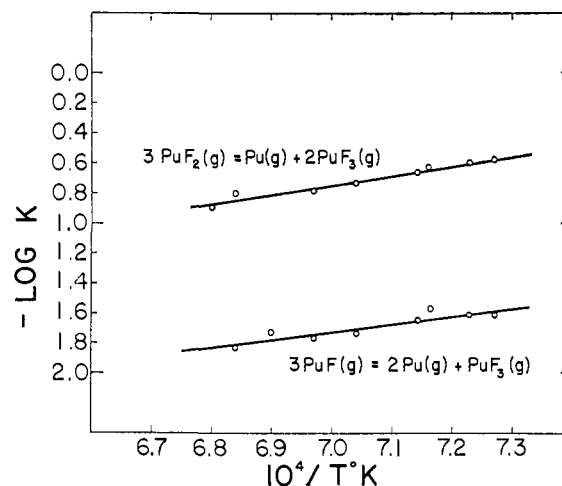

Figure 2. Temperature dependence of the equilibrium constants for reactions involving plutonium subfluorides.

The atomization energy and average bond energy of PuF$_3$(g) together with the dissociation energy of PuF(g) are listed in Table III and compared with published values for the group IIIa trifluorides and for various lanthanide trifluorides.