

VAPOR PRESSURE OF PROMETHIUM TRIFLUORIDE

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(Received 7 May 1988)

ABSTRACT

The vaporization of promethium trifluoride has been studied by Knudsen effusion–mass spectrometry. The equilibrium vapor pressure of PmF_3 over $(\text{Pr}_{1/3}\text{Pm}_{1/3}\text{Sm}_{1/3})\text{F}_3$ was measured relative to those of the other components (PrF_3 and SmF_3) over the temperature range of 1100–1280 °C. The vaporization behavior of PmF_3 was found to be very similar to that of PrF_3 . The results obtained in this study are tabulated and are discussed in terms of the promethium fluoride vaporization thermodynamics.

INTRODUCTION

The lanthanide element promethium does not occur in nature but is obtained by fission or other nuclear reactions. The radioactivity and scarcity of its available isotopes have discouraged investigations of the physicochemical properties of promethium and its compounds. The first study of promethium fluoride (PmF_3) was carried out by Weigel and Scherer [1] as part of a series of investigations to characterize the basic chemistry of promethium. They have described the preparation and structural characterization of several promethium halides and oxyhalides. The results of these and other studies have demonstrated that the basic chemistry of promethium is consistent with the relevant systematics established previously for the other lanthanide elements. It was the goal of this work to extend our understanding of the chemistry of promethium and its relationship to the other lanthanide elements through determination of the high temperature behavior of its trifluoride.

Our capability to handle highly radioactive materials and access to a supply of promethium-147 have allowed the investigation of the high temperature vaporization of promethium fluoride. A Knudsen effusion–mass spectrometric technique previously used to determine the relative vapor pressures/enthalpies of vaporization of other lanthanide fluorides [2] readily accommodates milligram-sized samples and has been applied to studying the vaporization of promethium fluoride. The relative vapor pressure of each

component of the ternary mixed fluoride system $(\text{Pr}_{1/3}\text{Pm}_{1/3}\text{Sm}_{1/3})\text{F}_3$ were determined simultaneously and the published thermodynamic quantities for the vaporization of PrF_3 were used to derive the corresponding values for PmF_3 . The results are discussed in relation to the high temperature vaporization properties of other lanthanide fluorides.

EXPERIMENTAL

Fluoride preparation and characterization

The fission product promethium-147 used in this work β decays to samarium-147 with a 958 day half-life. The separation of 3 mg of ^{147}Pm from its ^{147}Sm daughter was by high pressure cation exchange using the α -hydroxyisobutyric acid method [3]. A separation of Pm and Sm on a multi-gram scale has been described recently [4]. In the present work, a thin window β counter was used to monitor each drop of effluent from a 6 mm outer diameter heated cation exchange column. The first 15% of the Pm eluant was rejected to minimize the Sm content of the Pm product. The final purification of the Pm fraction from the complexing agent and other impurities was by two consecutive HCl cation exchange treatments, which produced a promethium chloride solution as the final product.

To allow a quantitative determination by spark source mass spectrometry of the separation of the promethium from its isobaric samarium daughter, the 3 mg sample of $\sim 75\%$ ^{147}Pm – $\sim 25\%$ ^{147}Sm was spiked with 500 μg of ^{152}Sm (approximate composition before separation: 62% ^{147}Pm –21% ^{147}Sm –17% ^{152}Sm). After separation, spark source mass spectrographic analysis of a portion of the promethium fraction indicated a ^{152}Sm content of < 10 ppm; this result demonstrated an effective Pm–Sm separation and implies a ^{147}Sm content of < 12 ppm at separation. The two PmF_3 vaporization experiments, denoted as PmF_3 –A and PmF_3 –B, were performed respectively 6 and 10 days after the final separation/purification.

Since the ^{147}Sm found in naturally occurring samarium (15% isotopic abundance) would also interfere with the mass spectral study of the ^{147}Pm component of the mixed fluoride, $^{152}\text{Sm}_2\text{O}_3$ (98.3% isotopic purity; 0.2% ^{147}Sm , 0.2% ^{148}Sm , 0.3% ^{149}Sm , 0.2% ^{150}Sm and 0.8% ^{154}Sm) was dissolved in HCl and used as the source of samarium for preparing the ternary fluoride. Normal praseodymium consists of 100.0% ^{141}Pr and commercial PrCl_3 (99.9%) was the source of Pr for the ternary mixed fluoride. Thus, as opposed to the Sm component, the Pm and Pr components of the ternary fluoride were monoisotopic. The ^{147}Sm content of the mixture, which would interfere with the ^{147}Pm mass spectral measurements, was the sum of that generated by decay of the ^{147}Pm plus that added as an isotopic impurity in the ^{152}Sm source. Thus, for the PmF_3 –A and PmF_3 –B samples, the ^{147}Sm contribution to the total mass-147 content of the samples was 0.6% and 0.9%

respectively at the time of the high temperature mass spectral measurements.

The ternary mixed fluoride ($\text{Pr}_{1/3}\text{Pm}_{1/3}\text{Sm}_{1/3}\text{F}_3$) was prepared from an aqueous chloride solution containing equimolar amounts (to within 1%) of Pr^{3+} , Pm^{3+} and Sm^{3+} (~ 2 mg of each lanthanide). The fluoride was precipitated from this solution by addition of HF; after air drying this material was heated with F_2 at 300°C for 2 days to ensure complete fluorination and dehydration.

Both the original ternary fluoride preparation and the residue remaining in the Knudsen cell after each high temperature study were analyzed by conventional X-ray diffraction (XRD) techniques using 114.6 mm diameter Debye-Scherrer powder cameras and Mo $K\alpha$ radiation. Refined lattice parameters were obtained by a least squares fit to the indexed diffraction lines [5].

Knudsen effusion-mass spectrometry

Approximately 3 mg of the mixed fluoride preparation (i.e. ~ 1 mg of each of the components PrF_3 , PmF_3 and SmF_3) was used for each of the two vapor pressure experiments. The tantalum Knudsen cells had an internal volume of 10 mm^3 , an orifice area of 0.02 mm^2 and a length/diameter ratio of 2. The cell bottom area (approximately equivalent to sample surface area) was about 400 times the area of the effusion orifice. Based upon the reported vapor pressure of PrF_3 [6] and assuming comparable vapor pressures for PmF_3 and SmF_3 , the total pressure in the cell during the experiments was always below 0.1 Torr, establishing molecular flow conditions.

Details of the quadrupole mass spectrometer and the experimental configuration have been given in [2]. Temperature measurements were made with a type-K (chromel/alumel) thermocouple, which was calibrated by observation of the melting points of high purity gold (m.p. = 1064°C) and lanthanum (m.p. = 921°C) metals contained in an open tantalum cell (no lid) in the identical experimental configuration. The observed melting point of each pure metal was within 10°C of its accepted value and no corrections were applied to the measured temperatures in the experiments. The reported temperatures are considered accurate to $\pm 15^\circ\text{C}$ on an absolute basis, with the relative values being considerably more precise. An ionizing electron energy of 70 eV was used for most of the measurements; this energy was varied from this value only for ionization efficiency determinations. The reported ion intensities correspond to the attenuation of particular mass (m/z) peak upon insertion of a shutter between the mass spectrometer ionization chamber and the effusion orifice.

RESULTS AND DISCUSSION

High temperature vaporization studies of PmF_3 were carried out using a ($\text{Pr}_{1/3}\text{Pm}_{1/3}\text{Sm}_{1/3}\text{F}_3$) complex fluoride. Powder XRD patterns obtained for

this mixed trifluoride resembled closely those reported for trigonal LaF_3 -type PrF_3 [7], PmF_3 [1] and SmF_3 [8]. Hexagonal lattice parameters of $a_0 = 7.018(2)$ Å and $c_0 = 7.179(3)$ Å were derived for $(\text{Pr}_{1/3}\text{Pm}_{1/3}\text{Sm}_{1/3})\text{F}_3$; as expected, these values are close to those of NdF_3 [9] and PmF_3 [1]. No splitting of the diffraction lines could be detected in the films, implying that the mixed trifluoride was a homogeneous, single phase material.

After completion of the vaporization experiments the Knudsen cells were opened and a dark red-orange colored residue was found inside each. These residues were composed of both unvaporized material remaining on the bottom of the cell and material which had vaporized and redeposited as crystals on the inside of the cell lid. Powder XRD analysis of these materials identified both as trigonal, LaF_3 -type LnF_3 . Although the measured lattice parameters were approximately the same as those derived for the $(\text{Pr}_{1/3}\text{Pm}_{1/3}\text{Sm}_{1/3})\text{F}_3$ starting material, the very spotty nature of the diffraction lines precluded obtaining parameters accurate enough to infer the exact composition of the residue. The physical appearance of the residues in the bottoms of the cells showed that fusion of the fluoride samples had not occurred during the experiments, and the measurements reported here are thus considered to refer to a solid phase of $(\text{Pr}_{1/3}\text{Pm}_{1/3}\text{Sm}_{1/3})\text{F}_3$. Greis and Cader [10] raise the possibility that high-temperature (second-order) structural transformations of the light lanthanide trifluorides may occur. Since our XRD analyses refer to the room temperature samples, the high-temperature measurements may have been of the high-temperature crystal modification which they propose; their thermal analysis results suggest that the enthalpy associated with this transformation is rather small and vaporization enthalpies should thus be affected only minimally.

Two vaporization experiments, PmF_3 -A and PmF_3 -B, were performed with the $(\text{Pr}_{1/3}\text{Pm}_{1/3}\text{Sm}_{1/3})\text{F}_3$ sample. Shutterable mass spectral peaks were measured over the temperature ranges of 1118–1254°C (PmF_3 -A) and 1104–1281°C (PmF_3 -B). Intensities of peaks due to the Ln^+ , LnF^+ , LnF_2^+ , and LnF_3^+ ion fragments were measured; of all such species which could be derived from $\text{Ln} = {}^{141}\text{Pr}$, ${}^{147}\text{Pm}$ and ${}^{152}\text{Sm}$, only the peak corresponding to the ${}^{152}\text{SmF}_3^+$ (209 amu) ion was not measured due to interference from relatively intense Pb^+ (206–208 amu) peaks in that mass region (the lead was present as an impurity in the vacuum chamber).

Figure 1 shows a mass spectrum over the mass range which includes the three LnF_2^+ ion fragments derived from the vaporization of $(\text{Pr}_{1/3}\text{Pm}_{1/3}\text{Sm}_{1/3})\text{F}_3$. Also evident in this mass spectrum are less intense peaks attributed to YbF^+ , which remained from a previous high temperature vaporization experiment with ytterbium. Assignment of these peaks to YbF^+ is substantiated both by agreement of their relative intensities with the abundances of the naturally occurring Yb isotopes and by observation of the corresponding Yb^+ and YbF_2^+ peaks. Since the ${}^{171}\text{Yb}^+$ and ${}^{171}\text{YbF}^+$ species contribute to the mass peaks corresponding to ${}^{152}\text{SmF}^+$ (171 amu) and

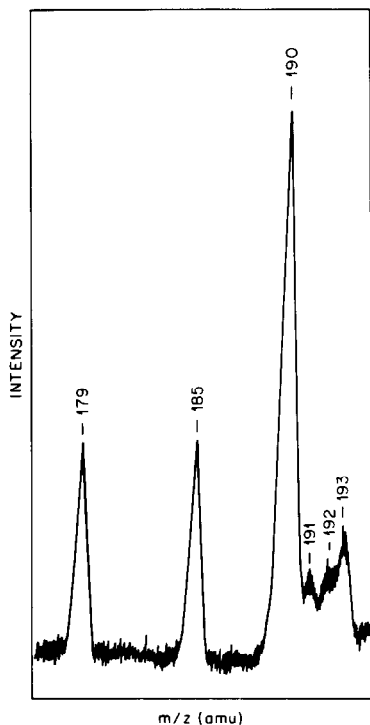


Fig. 1. Mass scan taken during experiment PmF_3 -A. Range = 177-194 amu, sample temperature = 1250 °C. The peak assignments are as follows: 179, PrF^+ ; 185, PmF^+ ; 190, $\text{SmF}_2^+ + {}^{171}\text{YbF}^+$; 191, ${}^{172}\text{YbF}^+$; 192, ${}^{173}\text{YbF}^+$; 193, ${}^{174}\text{YbF}^+$.

${}^{152}\text{SmF}_2^+$ (190 amu) respectively it was necessary to subtract the contributions of the ${}^{171}\text{Yb}$ -containing ions from the measured (shutterable) intensities of these peaks to obtain the component of the signal attributable to the ${}^{152}\text{Sm}$ -containing ions. Ytterbium-174 is the most abundant (31.8%) Yb isotope and by measuring the shutterable intensities due to its ion fragments it was possible to derive the contribution of the ${}^{171}\text{YbF}_x^+$ ion fragments (${}^{171}\text{Yb}$ has 14.3% isotopic abundance) to the SmF_{x+1}^+ ion peaks; the mass spectral intensities of the YbF_x^+ ion relative to the corresponding ${}^{152}\text{SmF}_{x+1}^+$ ion was typically as suggested by the mass spectrum in Fig. 1. The intensities measured for the ${}^{147}\text{PmF}_x^+$ mass peaks were not adjusted for the contribution from the ${}^{147}\text{SmF}_x^+$ content since the amount of ${}^{147}\text{Sm}$ in the mixed fluoride at the time of the measurements was less than 1% of that of ${}^{147}\text{Pm}$.

The mass spectral intensities measured for peaks assigned to ${}^{141}\text{Pr}$ -, ${}^{147}\text{Pm}$ - or ${}^{152}\text{Sm}$ -containing species are given in Table 1; these data are listed in the chronological order in which they were obtained. Although most of the data are for the LnF_2^+ ion fragments, intensities were also measured for other LnF_x^+ ion fragments ($x = 0, 1$ or 3), and values for $I[\text{LnF}_x^+]/I[\text{LnF}_2^+]$ (or $R[\text{LnF}_x^+]$) were derived and are listed in Table 2. That the intensities of

TABLE 1

Measured ion intensities ^a

m/z (amu) ^b	T (°C)	I^+ (pA)	m/z (amu) ^b	T (°C)	I^+ (pA)
PmF ₃ -A					
179	1162	3.5	190	1199	16.4
185	1159	1.6	179	1179	5.4
179	1168	4.5	185	1178	4.0
185	1168	1.8	190	1179	11.4
179	1170	5.5	179	1168	3.6
185	1170	2.8	185	1167	3.1
179	1187	8.0	179	1161	3.5
185	1187	3.8	185	1160	2.8
190	1187	8.1	179	1143	2.2
179	1206	12.5	185	1143	1.3
185	1205	6.5	190	1143	4.8
190	1206	14.8	179	1133	1.8
179	1222	17.0	185	1132	1.3
185	1223	10.5	190	1132	2.4
190	1222	26.3	190	1132	2.4
179	1247	28.0	185	1118	1.1
185	1248	17.5	190	1118	2.1
190	1249	40.0	179	1127	1.4
160	1248	16.5	185	1127	1.0
166	1248	5.5	190	1128	2.6
171	1249	7.3	179	1134	2.0
160	1251	16.5	185	1134	1.5
166	1250	5.0	190	1133	2.9
171	1251	7.4	179	1143	2.1
141	1250	31.0	185	1143	2.0
147	1250	14.5	190	1147	5.8
152	1250	10.5	179	1155	3.4
160	1250	17.0	185	1157	3.2
166	1250	5.0	190	1155	6.8
171	1250	6.9	179	1171	4.4
179	1247	25.5	185	1170	3.2
185	1247	21.0	190	1168	9.3
190	1252	45.3	179	1180	5.0
179	1249	27.0	185	1181	4.7
185	1247	20.0	190	1181	13.0
190	1251	46.2	179	1188	6.3
179	1239	20.5	185	1190	6.0
185	1238	15.5	190	1185	15.7
179	1231	17.5	179	1193	7.3
185	1229	14.5	185	1194	6.3
190	1230	36.3	190	1193	18.8
179	1217	13.5	179	1207	9.8
185	1216	9.5	185	1205	8.5
190	1216	25.6	190	1203	25.8
179	1198	8.5	179	1214	10.8
185	1200	6.5	185	1214	9.5

TABLE 1 (continued)

m/z (amu)	T ($^{\circ}\text{C}$)	I^+ (pA)	m/z (amu)	T ($^{\circ}\text{C}$)	I^+ (pA)
PmF₃-A					
190	1213	29.8	147	1236	5.0
179	1224	13.5	152	1236	4.0
185	1222	12.5	160	1236	8.0
190	1220	35.2	166	1236	3.0
179	1238	17.0	171	1236	2.0
185	1239	18.5	179	1236	14.0
190	1239	47.6	185	1236	16.2
179	1253	23.3	141	1237	18.8
185	1251	23.0	147	1237	9.3
190	1251	55.4	152	1237	7.0
160	1252	12.1	160	1231	10.0
166	1253	4.8	166	1231	5.0
171	1254	5.8	171	1231	4.5
141	1247	24.3	179	1234	16.0
147	1247	12.0	185	1234	21.0
152	1247	8.8	190	1234	45.7
198	1241	20.0	179	1248	20.5
179	1240	18.5	185	1250	29.5
185	1240	19.8	190	1250	54.1
190	1238	47.5	179	1242	17.0
			185	1242	24.0
			190	1242	49.8
PmF₃-B					
185	1104	0.8	179	1226	12.0
185	1123	1.4	185	1226	17.0
185	1137	1.7	179	1228	12.1
185	1157	2.6	185	1229	18.7
190	1157	5.7	190	1229	43.7
179	1162	4.4	179	1219	11.0
185	1162	2.8	185	1219	14.5
190	1162	7.5	190	1220	37.7
179	1171	4.8	179	1211	8.5
185	1171	3.8	185	1211	11.8
190	1173	10.4	190	1211	32.8
179	1190	7.0	179	1194	5.8
185	1190	5.5	185	1194	8.1
190	1189	14.8	190	1194	22.3
179	1197	7.5	179	1175	3.8
185	1196	6.0	185	1174	5.0
190	1196	17.2	190	1174	14.0
179	1206	8.3	179	1159	2.8
185	1204	6.8	185	1158	3.3
190	1204	21.5	190	1158	9.1
179	1216	9.8	179	1141	2.0
185	1216	10.8	185	1141	2.0
190	1216	28.3	190	1141	8.2
179	1228	12.5	179	1123	1.0
185	1228	14.0	185	1123	1.6
190	1228	36.4	190	1122	4.9
141	1236	14.0	179	1123	1.5

TABLE I (continued)

m/z (amu)	T ($^{\circ}\text{C}$)	I^+ (pA)	m/z (amu)	T ($^{\circ}\text{C}$)	I^+ (pA)
185	1123	1.7	179	1258	21.4
190	1123	4.4	185	1258	37.6
179	1135	1.4	190	1257	87.9
185	1136	2.0	179	1269	24.8
190	1137	6.5	185	1269	49.6
179	1152	2.2	190	1269	105.0
185	1152	2.8	179	1275	27.5
190	1153	8.9	185	1273	53.3
179	1161	3.0	190	1274	127.0
185	1160	3.3	179	1281	30.5
190	1159	10.5	185	1280	63.3
179	1168	3.4	190	1281	138.0
185	1170	4.8	179	1274	26.0
190	1170	13.0	185	1274	56.0
179	1178	4.5	190	1273	109.0
185	1177	5.4	179	1268	24.0
190	1177	15.6	185	1268	45.5
179	1187	5.0	190	1266	71.5
185	1188	7.2	179	1258	19.8
190	1187	18.8	185	1259	40.0
179	1201	6.8	190	1258	68.7
185	1200	9.3	179	1248	17.0
190	1200	25.1	185	1247	31.8
179	1217	9.0	190	1247	63.0
185	1215	14.0	141	1242	15.0
190	1216	35.7	147	1242	10.5
179	1222	10.0	152	1242	6.5
185	1222	16.2	160	1242	6.5
190	1222	40.8	166	1242	3.8
179	1236	13.2	171	1242	2.5
185	1235	22.0	179	1240	12.2
190	1236	51.4	185	1240	31.0
179	1246	18.0	190	1240	62.5
185	1246	29.1	198	1240	15.0
190	1246	73.4	204	1240	23.0

^a Shutterable ion intensities are listed in the chronological order in which they were obtained. The values for 171 and 190 amu are after subtraction of the contribution from Yb^+ and YbF^+ , respectively (see text).

The observed ion-fragment masses (m/z in amu) have been assigned as follows: 141, Pr^+ ; 147, Pm^+ ; 152, Sm^+ ; 160, PrF^+ ; 166, PmF^+ ; 171, SmF^+ ; 179, PrF_2^+ ; 185, PmF_2^+ ; 190, SmF_2^+ ; 198, PrF_3^+ ; 204, PmF_3^+ .

PrF_3^+ and PmF_3^+ were found to be comparable with those of PrF_2^+ and PmF_2^+ was somewhat surprising in light of fragmentation patterns found in other investigations [11]. Absolute appearance potentials were not determined but relative values measured for PrF_2^+ , PmF_2^+ and SmF_2^+ were

TABLE 2

Trifluoride ion-fragment intensities relative to LnF_2^+ ^a

Ion Fragment	$I[\text{LnF}_x^+]/I[\text{LnF}_2^+]$
Pr^+	1.1 ± 0.1
PrF^+	0.59 ± 0.06
PrF_3^+	1.2 ± 0.2
Pm^+	0.46 ± 0.15
PmF^+	0.22 ± 0.06
PmF_3^+	0.7 ± 0.2
Sm^+	0.15 ± 0.07
SmF^+	0.10 ± 0.07

^a Measured using 70 eV ionizing electrons.

found to be similar. Values for PrF_3^+ and PmF_3^+ were also in accord with one another but were lower than those for the LnF_2^+ ion fragments. The ionization efficiency maximum for all three LnF_2^+ species was found to occur close to the 70 eV electron energy used for the measurements reported in Table 1.

Enthalpy of sublimation

The measured LnF_2^+ ion intensities are plotted as $-\ln\{I[\text{LnF}_2^+] \times T\}$ versus T^{-1} in Fig. 2 (PmF_3 -A) and Fig. 3 (PmF_3 -B). The LnF_2^+ data are plotted because they were the most complete set of measurements; the other LnF_x^+ ion fragments would yield comparable results. Using the relationship $P_i = k_i I[i^+] T$, and the van't Hoff equation, the points should fall on a nearly straight line with a slope corresponding to the trifluoride enthalpy of

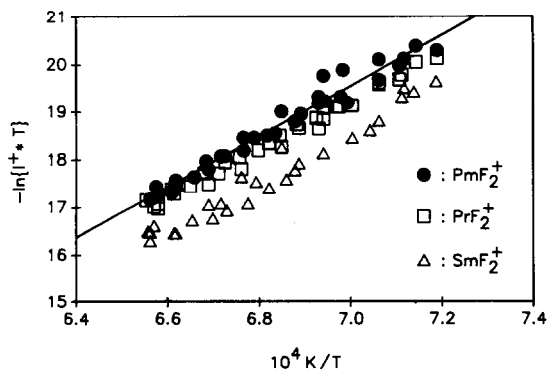


Fig. 2. Results of vaporization experiment PmF_3 -A. Indicated linear fit to PmF_2^+ data (●) gives $\Delta H_{\text{vap}}^{\text{II}}[\text{PmF}_3] = 105.7 \text{ kcal mol}^{-1}$.

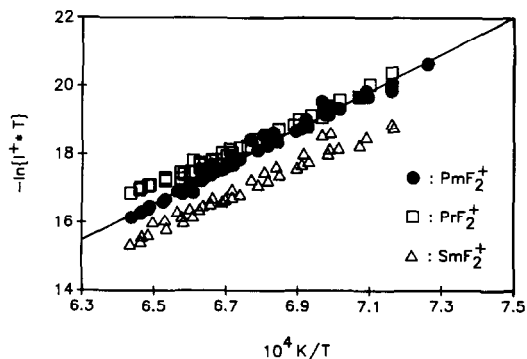


Fig. 3. Results of vaporization experiment $\text{PmF}_3\text{-B}$. Indicated linear fit to PmF_2^+ data (●) gives $\Delta H_{\text{vap}}^{\text{II}}[\text{PmF}_3] = 108.0 \text{ kcal mol}^{-1}$.

vaporization (divided by the ideal gas constant R). The least squares linear fits to the two PmF_2^+ data sets are shown in Figs. 2 and 3 and give $\Delta H_{\text{sub}}^{\text{II}}[\text{PmF}_3] = 107 \pm 10 \text{ kcal mol}^{-1}$ at 1200°C (average temperature). As discussed in ref. 2, it is considered that this sublimation enthalpy for PmF_3 in the mixed trifluoride closely represents that of pure PmF_3 (i.e. $\Delta H_{\text{mix}} \sim 0$).

A Third Law sublimation enthalpy for PmF_3 may be derived by estimating the relative vapor pressures of the components of the mixed fluoride from their ion-fragment intensities. The intensities for the SmF_x^+ species are less useful for this purpose than are those of the PrF_x^+ species because of (1) uncertainties introduced by correction of the $^{152}\text{SmF}_x^+$ data for the contribution from the $^{171}\text{YbF}_{x-1}^+$ background signal and (2) the possibility of incongruent vaporization of SmF_3 to form a partially reduced fluoride SmF_{3-z} ($0 < z < 1$) [12,13]. Samarium-152 fluoride was included in the mixed fluoride system primarily to confirm the assumed negligible contribution from $^{147}\text{SmF}_3$ to the $^{147}\text{LnF}_3$ vapor species (where Ln is primarily Pm): it was intended that the PrF_3 measurements would serve as the best calibrant for interpreting the PmF_3 results.

The pressure of PmF_3 over the mixed trifluoride is related to that of PrF_3 through the relationship

$$P[\text{PmF}_3]/P[\text{PrF}_3] = \{k[\text{PmF}_x^+]/k[\text{PrF}_x^+]\} \{I[\text{PmF}_x^+]/I[\text{PrF}_x^+]\}$$

Since the quadrupole sensitivity should be very similar for species which differ in mass by $< 5\%$, the calibration constant (k) ratio is dominated by the relative ionization cross sections $\sigma[\text{PrF}_3]$ and $\sigma[\text{PmF}_3]$. Values for $\sigma[\text{Ln}]$ are given by Mann [14] and those for Pr (10.91) and Pm (10.43) differ by less than 5%. The ionization cross section of a compound is typically considered to be some combination of those of its atomic components [15] (e.g. for a lanthanide trifluoride $\sigma[\text{LnF}_3] = a\sigma[\text{F}] + b\sigma[\text{Ln}]$), and $\sigma[\text{PrF}_3]$ and $\sigma[\text{PmF}_3]$ are thus taken here to be the same as one another to at least the extent of the agreement of the two $\sigma[\text{Ln}]$ values. However, the values cited in Table 2 for

the $R[\text{LnF}_x^+]$ ($R[\text{LnF}_x^+] \equiv I[\text{LnF}_x^+]/I[\text{LnF}_2^+]$) suggest rather different fragmentation patterns upon ionization of these three lanthanide trifluorides under our experimental conditions. To compensate for these differences, summed ion-fragment intensities must be considered; the total ion-fragment intensities are obtained by multiplying the measured $I[\text{LnF}_2^+]$ by the sum of the $R[\text{LnF}_x^+]$

$$\sum_{x=0}^3 I[\text{LnF}_x^+] = \sum_{x=0}^3 \{R[\text{LnF}_x^+]\} \{I[\text{LnF}_2^+]\}$$

Specifically, using the $R[\text{LnF}_x^+]$ from Table 2 for PrF_x^+ and PmF_x^+

$$\sum_{x=0}^3 I[\text{PrF}_x^+] = (3.9 \pm 0.4) I[\text{PrF}_2^+]$$

and

$$\sum_{x=0}^3 I[\text{PmF}_x^+] = (2.4 \pm 0.4) I[\text{PmF}_2^+]$$

The relationship between the pressures of PrF_3 and PmF_3 is thus

$$P[\text{PmF}_3]/P[\text{PrF}_3] = (0.62 \pm 0.15) I[\text{PmF}_2^+]/I[\text{PrF}_2^+]$$

Comparison of all of the measured $I[\text{PmF}_2^+]$ with isothermal $I[\text{PrF}_2^+]$ gives the following values for the ratio $I[\text{PmF}_2^+]/I[\text{PrF}_2^+]$: 0.77 ± 0.18 ($\text{PmF}_3\text{-A}$); 1.43 ± 0.41 ($\text{PmF}_3\text{-B}$), which yield a weighted average of 1.0 ± 0.4 . Using this average in the above equations gives $P[\text{PmF}_3]/P[\text{PrF}_3] = 0.7 \pm 0.4$ at 1200°C (average temperature).

By assuming that the sublimation entropies of PrF_3 and PmF_3 are similar ($\Delta\Delta S_{\text{sub}}[\text{PmF}_3 - \text{PrF}_3] \sim 0$), the above vapor pressure (equilibrium constant) ratio may be used to derive the sublimation enthalpy of PmF_3 relative to that of PrF_3

$$\begin{aligned} & -RT \ln \{ P[\text{PmF}_3]/P[\text{PrF}_3] \} \\ & = \Delta\Delta G_{\text{sub}}[\text{PmF}_3 - \text{PrF}_3] \sim \Delta\Delta H_{\text{sub}}[\text{PmF}_3 - \text{PrF}_3] = 1 \pm 3 \text{ kcal mol}^{-1} \end{aligned}$$

Three experimental studies of PrF_3 in the same temperature range as this investigation ($\sim 1200^\circ\text{C}$) have provided values for $\Delta H_{\text{sub}}[\text{PrF}_3]$: $82.3 \text{ kcal mol}^{-1}$ [16], $92.9 \text{ kcal mol}^{-1}$ [10] and $96.5 \text{ kcal mol}^{-1}$ [6]. Only the latter two values are consistent with the systematics of lanthanide fluoride sublimation thermodynamics, and in accordance with the critical assessment of Myers and Graves [17] the last value is selected as the best. Using $\Delta H_{\text{sub}}[\text{PrF}_3] = 96.5 \text{ kcal mol}^{-1}$ and our $\Delta\Delta H_{\text{sub}}[\text{PmF}_3 - \text{PrF}_3] = 1 \pm 3 \text{ kcal mol}^{-1}$ yields $\Delta H_{\text{sub}}[\text{PmF}_3] = 98 \pm 3 \text{ kcal mol}^{-1}$.

Combination of this Third Law result with the less reliable Second Law value of $107 \pm 10 \text{ kcal mol}^{-1}$ yields a weighted average of $\Delta H_{\text{sub}}[\text{PmF}_3] = 100 \pm 5 \text{ kcal mol}^{-1}$ at 1200°C . Since heat capacity and related data for

PmF_3 , as well as for other Pm-containing compounds, are not available an extrapolation of the enthalpy of sublimation to 298 K was not made.

CONCLUSION

Sublimation studies of the mixed ternary fluoride $(\text{Pr}_{1/3}\text{Pm}_{1/3}\text{Sm}_{1/3})\text{F}_3$ have shown the vapor pressure of PmF_3 to be close to that of PrF_3 . From Second and Third Law treatments of the results, a sublimation enthalpy was derived for PmF_3 at 1200°C: $\Delta H_{\text{sub}}[\text{PmF}_3] = 100 \pm 5 \text{ kcal mol}^{-1}$. The sublimation thermodynamics of PmF_3 have thus been shown to be consistent with the systematics previously established [2,17] for other lanthanide fluorides.

ACKNOWLEDGEMENT

This research was sponsored by the Division of Chemical Sciences, U.S. Department of Energy under contract DE-ACO5-84OR21400 with Martin Marietta Energy Systems, Inc.

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