Thermal Decomposition of Curium Tetrafluoride and Terbium Tetrafluoride

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The thermal decompositions of both curium and terbium tetrafluorides have been studied using mass spectrometry to monitor the effusate from a Knudsen cell containing the condensed fluoride. Curium tetrafluoride was found to decompose at 330–430°C in vacuum. A Second Law enthalpy of 26.3 ± 2 kcal/mole (at 370°C) is derived from van't Hoff plots of results obtained for the decomposition reaction:

$$CmF_4(s) \rightarrow CmF_3(s) + \tfrac{1}{2} F_2(g).$$

Decomposition fluorine pressures are derived and comparison is made with related studies of terbium tetrafluoride carried out in conjunction with the curium experiments. The results are compared both with data reported in the literature for lanthanide and actinide tetrafluorides and with predictions that have been made for CmF_4. © 1988 Academic Press, Inc.

Introduction

Several of the lanthanide and actinide elements form both a trifluoride and a tetrafluoride in the solid state. Their thermal decomposition process,

$$MF_4(s) \rightarrow MF_3(s) + \tfrac{1}{2} F_2(g), \qquad (1)$$
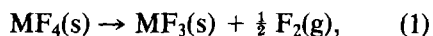
is especially informative because the tendency for this reaction to proceed provides an indication of the relative stabilities of the tetravalent and trivalent lanthanide/actinide species.

Specifically, the enthalpy associated with Reaction (1) (ΔH_d) is the difference between the heats of formation of the tri- and tetrafluorides:

$$\Delta H_d = \Delta H_f [MF_3] - \Delta H_f [MF_4].$$

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These enthalpies have been predicted or measured for several lanthanides and actinides as indicated in Table I (298 K values). The decomposition enthalpy of $TbF_4(s)$ has been measured directly by high-temperature study of Reaction (1) (*1*), while enthalpies of $CeF_4(s)$ (*2, 3*) and $UF_4(s)$ (*3*) have been derived from the results of independent thermochemical studies of the tri- and tetrafluorides. The remaining enthalpies of decomposition given in Table I are based upon predictions made for the heats of formation of the various trifluorides and/or tetrafluorides (*3, 4*). Consistent with the relatively large (positive) ΔH_d for CeF_4, UF_4, NpF_4, and PuF_4, high-temperature (congruent) vaporization studies of these tetrafluorides (*2, 5*) have indicated substantial thermal stability. Conversely, PrF_4 is especially difficult to pre-

TABLE I

LANTHANIDE/ACTINIDE FLUORIDE ENTHALPIES OF
FORMATION AND DECOMPOSITION

M	$-\Delta H_f[MF_4(s)]$	$-\Delta H_f[MF_3(s)]$	ΔH_d^a	Refs.
Ce	465[e] kcal/mol	407[e] kcal/mol	58[e] kcal/mol	(2, 3)
Pr	414[p]	404[e]	10[p]	(3, 4)
Tb	424[p]	408[e]	19[e]	(1, 3, 4)
U	457[e]	359[e]	98[e]	(3)
Np	448[p]	365[p]	83[p]	(3)
Pu	441[p]	379[e]	62[p]	(3)
Am	411[p]	384[p]	27[p]	(3)
Cm	404[p]	382[p]	22[p]	(3)
Bk	429[p]	378[p]	51[p]	(3)
Cf	388[p]	371[p]	17[p]	(3)

Note. [e] Experimental; [p] predicted.

pare and readily decomposes (6), in accord with its small predicted enthalpy (smaller values than that listed in Table I have been estimated for PrF_4 by others (4)).

It is evident from the values in Table I that the variations in the enthalpies for decomposition of lanthanide and actinide tetrafluorides are dominated by differences between the tetrafluoride heats of formation across these series. Differences between the trifluoride heats of formation are, in general, significantly smaller. The variations in enthalpies determined for Reaction (1) may thus be considered as indicative of the relative stabilities of the lanthanide/actinide tetravalent state.

Since tetrafluorides with small ΔH_d (e.g., PrF_4) decompose at low temperatures while those with large ΔH_d (e.g., CeF_4, UF_4, NpF_4, and PuF_4) vaporize congruently as MF_4 without substantial decomposition, those tetrafluorides with $\Delta H_d \cong 20$ kcal/mole are most amenable to direct study by Reaction (1). We have thus undertaken to investigate experimentally the decomposition of $CmF_4(s)$ and $TbF_4(s)$ by monitoring mass spectrometrically the effusate from a Knudsen cell containing $MF_4(s)/MF_3(s)$. The results of this work are discussed and compared with relevant experimental studies and predictions reported in the literature.

Experimental

Tetrafluoride Preparation and Analysis

The curium used in this study consisted of a mixture of 3% ^{246}Cm ($t_{1/2} = 4.8 \times 10^3$ years; α decay) and 97% ^{248}Cm ($t_{1/2} = 3.4 \times 10^5$ years; α decay) which was obtained as a product from the High Flux Isotope Reactor and Transuranium Processing Facility at the Oak Ridge National Laboratory. Spark-source mass spectrographic analysis of portions of the lot used for this work indicated a total metallic impurity level of less then 200 wt ppm. The starting material for the TbF_4 preparations was 99.9% commercial terbium nitrate salt.

The tetrafluorides of both curium and terbium were prepared by treating repeatedly (4–6 times) the respective trifluorides with fluorine in a nickel container at temperatures up to 450°C. The trifluorides were prepared via aqueous precipitation using HF. Details of the preparative technique are given in (7). Tetrafluoride preparations and the final products after high-temperature study were analyzed by conventional X-ray diffraction (XRD) using MoKα radiation and 114.6-mm-diameter Debye–Scherrer powder cameras.

Decomposition Studies

For the high-temperature studies, ~4 mg of the curium fluoride or ~10 mg of the terbium fluoride was contained in a nickel Knudsen cell which had a cylindrical orifice diameter of 0.15 mm ($L/r \cong 4$) and an internal volume of ~0.01 cm^3. These cells were fabricated entirely by mechanical machining. Sealing of the lid to the cell body was by a press fit of the close-tolerance lid lip against the 0.4-mm-thick cell wall. Orifice dimensions were determined from calibrated optical micrographs. A blank run with an empty Ni Knudsen cell was carried out to assure that it was not a source of mass spectral interference at elevated temperatures. In addition, one of the terbium

fluoride experiments was performed using a tantalum Knudsen cell (of the same dimensions). All handling of the tetrafluoride samples was carried out in a helium-filled glove box, except for the few minutes while the Knudsen cell (with lid on) was being loaded into the Knudsen effusion/mass spectrometric system.

The Knudsen effusion/mass spectrometric system used to monitor the identity and intensity of the decomposition/vaporization products was mounted in an α-containment (air atmosphere) gloved box and the Knudsen cells containing the fluorides were loaded into the vacuum chamber enclosing the Knudsen effusion/mass spectrometric system from within this box. Immediately after loading the Knudsen cell into it, the vacuum chamber was sealed and evacuated.

Heating of the Knudsen cell was accomplished with a tantalum-coil resistance furnace. Temperatures were measured with a type-K (chromel/alumel) thermocouple that was in direct contact with the Knudsen cell. Calibration of the temperature measurements was accomplished by observation of the melting points of Pb (m.p. = 328°C) and Al (m.p. = 660°C; the effect of possible Ta dissolution is discussed in (8)), metals contained in tantalum Knudsen cells (without lids) in the experimental configuration; appropriate corrections were applied to the measured experimental temperatures and the reported absolute temperatures are considered accurate to ±15°C (relative temperatures are significantly more accurate).

Background pressures were maintained below 10^{-7} Torr with a 330 liter/sec turbomolecular pump. The orifice of the Knudsen cell was centered (~7 cm) below the ionization chamber of a UTi 100 C (1–300 amu) quadrupole mass spectrometer. An ionizing electron energy of 70 eV was used for the measurements and the filtered ion currents (i.e., the ions emerging

from the quadrupole tuned to a particular m/z) were amplified with a Channeltron electron multiplier. The amplified currents were measured with a picoammeter, the 0- to 10-V output from which was recorded on a strip chart recorder. That portion of a mass peak deriving from the cell was discriminated from the background by "shuttering" the signal using an externally operated shutter located between the cell and the ionization chamber. The ability to "shutter" the beam arising from the cell was found to be especially important in the low mass range (e.g., 38 amu, F_2^+) where background signals were often significant; the shutterable F_2^+ signal could be as little as 1% of the total $m/z = 38$ amu signal. That portion of the ion current determined to derive from the effusate from the Knudsen cell is referred to as the "shutterable" signal.

It should be noted that the small amount of $^{248}CmF_4$ (and TbF_4) studied precluded detailed study of such effects as hysteresis and ionization efficiencies.

Results and Discussion

TbF$_4$ Decomposition

In conjunction with the study of curium tetrafluoride, the high-temperature decomposition/vaporization behavior of terbium fluorides was also investigated. The expected similarity between the decomposition behavior of $CmF_4(s)$ and $TbF_4(s)$ (see Table I) suggested terbium as a particularly appropriate choice here for the companion lanthanide study. Since the properties of lanthanide fluorides are better established than those of transplutonium fluorides, the results obtained with terbium tetrafluoride are presented first.

The terbium tetrafluoride preparations were analyzed by XRD prior to the high-temperature decomposition experiments and were found to be ZrF_4-type (mono-

clinic) TbF_4 (9). Residues analyzed after these experiments were determined to be YF_3-type (orthorhombic) TbF_3 (10).

Two experiments on $TbF_4(s)$ using nickel cells were carried out. In both cases, the decomposition generated a shutterable F_2^+ peak below 400°C; in one case only a limited amount of data were collected before the tetrafluoride sample was depleted. Associated with the appearance of shutterable fluorine in these experiments were partially shutterable peaks which corresponded to ion fragments of TaF_5. This result has been interpreted as reflecting reaction of some of the fluorine effusate with the tantalum heater coil or other tantalum components. The location of one such (broad due to loss of instrument resolution at high m/z) peak at 219 amu (TaF_2^+) precluded attempts to detect the TbF_3^+ (216 amu) fragment, which would have been indicative of the congruent vaporization of TbF_4. The complete set of fluorine vapor pressure measurements over $TbF_4(s)$ provided data between 390 and 515°C; all of the data obtained from this sample prior to sample depletion are shown in Table II, in the order in which the data points were obtained. Using the relation, $P_i = k_{i+} \times I_{i+} \times T$ (where $i+$ is some ion fragment of vapor species i, and k is the instrument sensitivity; the instrument sensitivity was not determined for these experiments, and the results suggest that it varied significantly from experiment to experiment), and the van't Hoff equation, the temperature dependence of our F_2^+ measurements from this latter sample was used to obtain a Second Law enthalpy of decomposition (Reaction (1)) through the following:

$$d\ln K_{eq}/d(1/T) = d\ln P_{F_2}^{1/2}/d(1/T)$$
$$= \tfrac{1}{2} d\ln[(I_{F_2}^+)(T)]/d(1/T) = -\Delta H_d/R$$

In Figure 1 is shown a van't Hoff plot of our data for the decomposition of $TbF_4(s)$ to $TbF_3(s)$. The indicated least-squares linear

TABLE II

KNUDSEN EFFUSION/MASS SPECTROMETRIC RESULTS FOR THE DECOMPOSITIONS OF $TbF_4(s)$ AND $CmF_4(s)$ AND THE VAPORIZATION OF $TbF_3(l)$

Sample/Ion	T (°C)	I (pA)
TbF_4/F_2^+	390	11.5
	398	22.4
	411	48.9
	422	88.6
	425	97.6
	422	127
	432	240
	437	279
	432	215
	455	304
	463	538
	472	948
	492	2040
	515	3190
TbF_3/TbF_2^+	1218	5.89
	1266	15.8
	1307	30.1
	1348	51.9
	1338	48.7
	1382	88.2
	1340	50.7
	1305	30.8
	1266	17.0
	1224	7.61
$CmF_4(A)/F_2^+$	333	3.0
	347	7.0
	366	28
	379	65
	395	170
	410	300
	430	800
$CmF_4(B)/F_2^+$	332	0.5
	342	1.5
	352	3.3
	361	6.5
	371	12.5
	379	19.5
	389	37
	400	63
	409	90

fit to the data gave a decomposition enthalpy of 23.7(±3) kcal/mole at 450°C (average temperature). Our results for the thermal decomposition of $TbF_4(s)$ may be
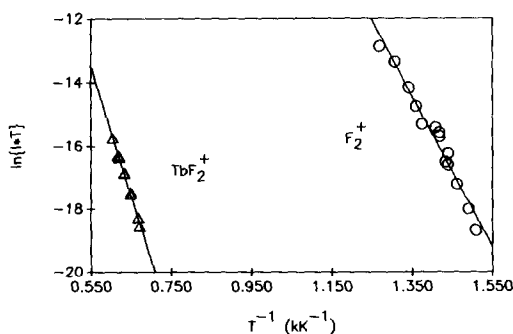
FIG. 1. Results for $TbF_4(s)$ decomposition ($\bigcirc$) and $TbF_3(l)$ congruent vaporization ($\triangle$). The indicated linear fits give the following enthalpies: $\Delta H_d[TbF_4(s)]$ = 23.7(±3) kcal/mole and $\Delta H_{vap}[TbF_3(l)]$ = 81.4(±5) kcal/mole.

compared with those of Nikulin *et al.* (*1*) where the decomposition was similarly observed in the range 394–507°C, and an enthalpy of 19.1 $\pm$ 2.4 kcal/mole (at 298 K) was derived.

When a tantalum cell was used to contain $TbF_4(s)$, the shutterable mass spectrum was dominated by peaks considered to be ion fragments of the volatile TaF_5 species. Although a shutterable F_2^+ peak was observed (at ~450°C), the primary TaF_5 ion fragment peak, TaF_4^+ (257 amu), was over 20 times more intense (the shutterable F^+ (19 amu) peak was always much smaller than the corresponding F_2^+ peak). Thus most of the fluorine released due to the decomposition of $TbF_4(s)$ apparently generated tantalum pentafluoride prior to effusion from the cell. The possibility of the solid-solid reaction, $5\ TbF_4(s)\ +\ Ta(s)\ \rightarrow\ 5\ TbF_3(s)\ +\ TaF_5(g)$, discouraged the use of the TaF_x^+ data as a direct probe of the thermal decomposition of $TbF_4(s)$. The F_2^+ data was also unlikely to be representative of equilibrium fluorine partial pressures under these conditions.

The terbium fluoride in a tantalum cell was subsequently heated to temperatures well above the region of $TbF_4(s)$ decomposition to investigate the congruent vaporization of the TbF_3 product. Shutterable peaks corresponding to the dominant TbF_3

fragment ion, TbF_2^+ (197 amu), were measured between 1110 and 1380°C. Data obtained for TbF_3 above the reported trifluoride melting point of 1172°C (*11*) are included in Table II and Fig. 1 and the indicated linear fit gives a Second Law enthalpy of vaporization of 81.4 $\pm$ 5 kcal/ mole for $TbF_3(l)$ at 1300°C (average temperature). These latter results are included here primarily to demonstrate the continuity of the terbium fluoride vaporization processes, but they can be compared to data published for TbF_3. The ΔH_{vap} obtained here compares reasonably well with values reported for $TbF_3(s)$ (*12*) (~100 kcal/ mole at 1100°C) when the difference between the temperature ranges, and the heat of fusion ($\Delta H_{fus}[LnF_3]$ $\cong$ 13 kcal/mole for other lanthanide trifluorides (*13*)) are taken into account.

CmF_4 Decomposition

Four curium fluoride samples were studied using nickel effusion cells. XRD analysis of the four tetrafluoride preparations before the high-temperature mass spectrometric studies showed two of them were mixtures consisting of comparable amounts of ZrF_4-type (monoclinic) CmF_4 (*14*) and LaF_3-type (trigonal) CmF_3 (*15*), while the remaining two preparations were primarily CmF_3. The presence of CmF_3 in the starting material does not affect the decomposition equilibrium (CmF_3 will be generated and must be present at equilibrium) but does imply a smaller amount of CmF_4 available for study prior to depletion of the sample. Residues in the cells analyzed by XRD after the decomposition studies were identified as LaF_3-type CmF_3.

In each of the four $CmF_4(s)$ runs, a shutterable F_2^+ peak was first detected by ~340°C and disappeared by ~430°C, indicating tetrafluoride depletion. Only those two samples where $CmF_4(s)$ was a major component provided sufficient equilibrium measurements for deriving reliable Second

Law enthalpies. Chronologically, these two experiments were denoted A and B; the cell used for run A was emptied and reused for run B, with the intent that the cell interior would be at least partially passified by fluorine prior to the second run. Measurements of the shutterable difluorine ion current ($I[F_2^+]$) were made at temperatures between 333 and 430°C during run A, and between 332 and 409°C during run B. All of the predepletion data are shown in chronological order in Table II. The results from both of these experiments are represented as van't Hoff plots in Fig. 2. The least-squares linear fits to the data sets are also shown and yield decomposition enthalpies of 25.4($\pm$2) kcal/mole (run A) and 27.7($\pm$3) kcal/mole (run B); we thus report a Second Law enthalpy for the decomposition of $CmF_4(s)$ to $CmF_3(s)$ of 26.3 $\pm$ 2 kcal/mole at 370°C (average temperature). The two extreme points from the data set shown in Fig. 2 for CmF_4 sample B ($\triangle$'s) deviate slightly from the linear fit to give an appearance of possible curvature. This may be related to initial sample depletion (prior to the subsequently observed catastrophic depletion) at the highest temperature but the effect is rather small (especially given the <100°C temperature range of the data) and the best linear fit through all of the data has been used. Using the ΔC_p for the corresponding decomposition of PuF_4 (5) as the ΔC_p for CmF_4 ($\Delta C_p \cong -1.3$ cal/mole · K at 500 K), a 298 K enthalpy of 26.8 kcal/mole can be derived for the decomposition of $CmF_4(s)$. As this suggests, the temperature dependence of this enthalpy is expected to be rather small.

The 300 amu mass limit of the quadrupole used in this work precluded searching for the $^{248}CmF_3^+$ (305 amu) primary ion fragment of the CmF_4 vapor species which would result from the congruent vaporization of the tetrafluoride. However, based upon vaporization studies of other actinide tetrafluorides (e.g., $P^0[AmF_4] = 7 \times 10^{-8}$

Torr at 450°C (5)), the partial pressure of $CmF_4(g)$ over $CmF_4(s)$ would be expected to be much lower than the decomposition fluorine partial pressure.

To minimize the possibility of any alteration of the decomposition equilibrium via chemical interactions with gaseous species, no internal calibrant material was introduced into the cells. Although mass spectrometer calibration constants (k in $P = k \times I \times T$) were thus not determined (and varied significantly from run to run as the data separation between runs A and B in Fig. 2 illustrates), the fluorine pressures over $TbF_4(s)$ and $CmF_4(s)$ may be estimated. To derive fluorine pressures from the Second Law decomposition enthalpy reported here for $CmF_4(s)$, the decomposition entropy, ΔS_d, may be estimated by assuming that the only difference between the entropies for the PuF_4 and CmF_4 decompositions is due to the $5f^n$ magnetic contribution (16). Such a treatment generates $\Delta S_{d,700 K}[CmF_4] = 22.9$ cal/mole K, and $P_{700 K}[F_2/CmF_4(s)] = 3 \times 10^{-4}$ Torr. This latter value is consistent with the observed depletion of the $CmF_4(s)$ samples in the experiments.

Conclusion

The most significant findings of this study are that curium tetrafluoride decomposes in
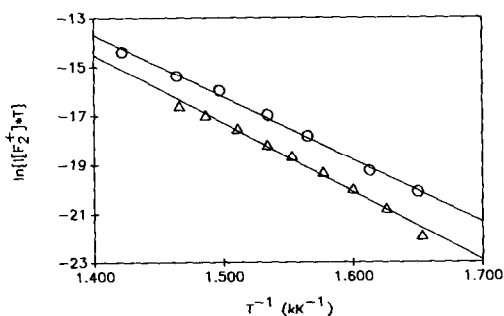

FIG. 2. Results for $CmF_4(s)$ decomposition. The indicated linear fits give the following values for $\Delta H_d(CmF_4)$: 25.4($\pm$2) kcal/mole (O; run A) and 27.7($\pm$3) kcal/mole ($\triangle$; run B).

vacuum at temperatures in the region of 400°C and that $CmF_4(s)$ is only slightly more stable ($\Delta\Delta H_d[CmF_4-TbF_4] \cong 3 \pm 2$ kcal/mole) to decomposition than is $TbF_4(s)$. Results reported here for the decomposition of $TbF_4(s)$ and $CmF_4(s)$ to their respective trifluorides are consistent with one another. The decomposition enthalpies derived here are approximately 4 kcal/mole larger than predicted for $CmF_4(s)$ and 5 kcal/mole larger than previously derived for $TbF_4(s)$. Although these differences are small relative to the magnitude of the $MF_4(s)$ and $MF_3(s)$ heats of formation (~1%), they suggest a slightly greater stability of the tetravalent curium and terbium fluorides than was expected from the values given in Table I.

Acknowledgments

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