HIGH TEMPERATURE VAPORIZATION/DECOMPOSITION OF LANTHANIDE AND ACTINIDE FLUORIDES

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The Knudsen effusion-mass spectrometric technique has been used in this laboratory to study the congruent vaporization and thermal decomposition of several lanthanide and actinide fluorides. Reported here are the results of experiments which were performed to establish the thermal stability of AmF$_4$(s) and CeF$_4$(s). The relative importance of the decomposition reaction,

$$MF_4(s) \rightarrow MF_3(s) + 1/2 F_2(g)$$

and the congruent vaporization process,

$$MF_4(s) \rightarrow MF_4(g)$$

upon heating of AmF$_4$(s) and CeF$_4$(s) are discussed.

INTRODUCTION

The thermal decomposition of solid lanthanide and actinide tetrafluorides is of interest as a direct indication of the relative stabilities of the tetravalent and trivalent lanthanide/actinide species in this environment. For those lanthanides/actinides known to form both a solid tetrafluoride and a solid trifluoride (Ce, Pr, Tb, U, Np, Pu, Am, Cm, Bk, and Cf), enthalpies have been measured or estimated for the decomposition reaction:

$$MF_4(s) \rightarrow MF_3(s) + 1/2 F_2(g) \quad [1]$$

$$\Delta H_d = \Delta H_f[MF_3] - \Delta H_f[MF_4] \quad [2]$$
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The values for $\Delta H_d$ range from less than 10 kcal/mol for PrF$_4$ (1,2) to almost 100 kcal/mol for UF$_4$ (1). Lanthanide/actinide tetrafluorides with small $\Delta H_d$ (PrF$_4$) are difficult to prepare and decompose at low temperatures (<100°C) (3) while those with the largest $\Delta H_d$ (UF$_4$, NpF$_4$, PuF$_4$) sublime prior to decomposition (4). The tetrafluorides of Tb, Am, Cm, Cf, and possibly Ce are expected to decompose in the temperature range of 200-1000°C and it is thus possible to directly study the decomposition reaction [1] for these elements. Recent investigations in this laboratory of the thermal stability of CmF$_4$($s$) and TbF$_4$($s$) will be reported elsewhere (5). Here we report the results of our study of the thermal decomposition of AmF$_4$($s$) and CeF$_4$($s$).

Americium tetrafluoride has been reported to thermally decompose according to reaction [1] above 650°C (6). Such behavior is in apparent conflict with thermodynamic quantities estimated for AmF$_3$($s$) and AmF$_4$($s$) (4) although more recent estimates (1) are in somewhat better accord with this unexpectedly low decomposition temperature. The suggestion of AmF$_4$($s$) decomposition by Chudinov and Choporov (6) was based upon unusual behavior in the measured AmF$_4$ vapor pressure above 650°C and it was considered desirable to confirm their interpretation of their observations by direct study of the fluorine evolution from americium tetrafluoride. We have thus undertaken to monitor the evolution of F$_2$(g) from samples of AmF$_4$($s$) using the Knudsen effusion-mass spectrometric method.

Although several experimental studies of CeF$_4$($s$) sublimation/decomposition have been reported (7 and references therein), there remains controversy as to the widely disparate decomposition temperatures (<400 to >800°C) reported by the various groups. In conjunction with our transplutonium studies, we have thus also undertaken to clarify the thermal decomposition behavior of cerium tetrafluoride.

**EXPERIMENTAL**

*Fluoride Preparation and Containment*

The $^{243}$Am isotope used in this work was obtained as a product from the High Flux Isotope Reactor and Transuranium Processing Facility at the Oak Ridge National Laboratory; greater than 99.98% of the americium was the $^{243}$Am isotope ($t_1/2 = 7370$ years; $\alpha$-decay). The starting material for the cerium fluoride preparations was 99.9% commercial cerium chloride salt.

The tetrafluorides of both americium and cerium 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 had been prepared by aqueous precipitation using HF. Further details of the preparative technique are given in (8). Tetrafluoride preparations as well as products residues after high temperature study were analyzed by conventional x-ray diffraction (XRD) using Mo-Kα radiation and 114.6 mm diameter Debye-Scherrer powder cameras.

Selection of container materials for high temperature fluoride decomposition studies is difficult due to the reactive nature of the liberated fluorine gas. The higher temperatures necessary for thermal decomposition of AmF₄(s) and CeF₄(s) (as compared with CmF₄(s) and TbF₄(s) (5)) necessitates especially cautious selection of materials for their containment. Nickel has generally been the material of choice for such studies but, as discussed below, certain complications were introduced by interactions when nickel was used, and thus other materials were also tried. Knudsen cell materials used were: (1) Nickel - Ni which was untreated or only mildly treated with aqueous HF at room temperature (no discernable difference was observed between the performance of untreated and mildly treated Ni); (2) Nickel - pre-fluorinated under the conditions used for the AmF₄(s)/CeF₄(s) preparations; (3) Tantalum; (4) Sapphire - Al₂O₃ cup in a tantalum cell with a tungsten screen over the cup to prevent spillage of the sample onto the Ta surface. A supplemental study of AmF₄(s) decomposition was carried out in a sealed quartz capillary. All the Knudsen cells all had an orifice diameter of 0.15 mm (with length/diameter ~2) and an internal volume of ~0.01 cm³. Some experiments (as noted) were carried out without a lid on the cell.

Approximately 5 mg of AmF₄(s) or 10 mg of CeF₄(s) was used for each experiment. All handling of the tetrafluoride samples was carried out in a helium atmosphere glove box except for the few minutes while the Knudsen cell was being loaded into the mass spectrometer system prior to evacuation.

Mass Spectrometry

The mass spectrometer system was mounted into the wall of an alpha-containment glove box (air atmosphere) and all sample loading was from within the box. A 330 lit/sec turbomolecular pump maintained the pressure in the vacuum chamber below 10⁻⁶ torr during the experiments.

Heating of the Knudsen cell was by a tantalum coil resistance furnace surrounding the tantalum cup in which the cell was contained. The cell rested on a type-K (chromel/alumel) thermocouple. Temperature measurements were calibrated by the observation
of the melting points of Pb° (m.p. = 328°C) and Al° (m.p. = 660°C) metals contained in tantalum cells in the experimental configuration. The temperatures reported here are considered to be accurate to within ±10°C.

The top of the cell was located 7 cm below the center of the ionization chamber of a UTi 100 C (1-300 amu) quadrupole mass spectrometer. The effusate was ionized with 70 eV electrons and the mass-filtered ions were detected and the currents amplified with a Channeltron electron multiplier. A shutter located between the cell and ionization chamber allowed that portion of a peak deriving from the cell to be discriminated. The ion fragment observations reported here refer to the "shutterable" signal and reflect decomposition/vaporization products from the cell.

RESULTS AND DISCUSSION

The results of the decomposition/vaporization experiments performed on americium tetrafluoride and cerium tetrafluoride are summarized in Table I. The starting fluoride samples for these investigations were analyzed by powder XRD and found to consist primarily of the tetrafluoride; relatively weak reflections assignable to the respective trifluorides were occasionally observed but the presence of AmF₃/CeF₃ should not affect these studies.

Cerium Tetrafluoride

As shown in Table I, three Knudsen effusion-mass spectrometry experiments were performed using nickel as the cell material. Nickel was chosen because of its resistance to attack by fluorine due to formation of a protective fluoride layer. Such cells were previously used successfully to monitor the fluorine generation from even smaller samples of CmF₄(s) and TbF₄(s) (5).

For all three sample, the CeF₃⁺ (197 amu) primary ion fragment of the CeF₄ vapor species (from CeF₄(s) congruent sublimation) was detected beginning at ~550°C. A van't Hoff plot of the results of one of these experiments is shown in Figure 1. The slope resulting from the low temperature data (X's) indicates a sublimation enthalpy of approximately 40 kcal/mol for CeF₄(s); this value is somewhat smaller than the corresponding values for other lanthanide/actinide tetrafluorides (4) and is more than 20 kcal/mol lower than that reported for CeF₃(s) in (7) but is not considered particularly accurate because of the limited temperature range of the data used (~100°C) and the possibility of sample depletion (due to tetrafluoride decomposition). The most significant aspect of the data
shown in Figure 1 is the indication of disappearance of CeF₄(g) (implying depletion of CeF₄(s)) above \( \approx 700 ^\circ C \) (this effect was also observed for the other two CeF₄ samples). As indicated in Table I, XRD analysis of the solid residue in one of the cells (there was a significant amount of residue in each case after the high temperature study) indicated that decomposition to CeF₃(s) had occurred below 750°C. That no shutterable F₂ signal was detected coincident with this decomposition indicates a reaction of the decomposition-generated fluorine with the nickel cell. This effect is due to the higher temperatures necessary for CeF₄(s) (and AmF₄(s)) decomposition (as compared with CmF₄(s) and TbF₄(s) (5)) and is consistent with the results for AmF₄(s) as described below.

Our observation of curium tetrafluoride thermal decomposition in the region of 700°C is in contrast to the results of (7) which suggest stability to significantly higher temperatures. Attempts are continuing in this laboratory to develop a Knudsen cell more suitable for direct monitoring of fluorine generated from cerium tetrafluoride thermal decomposition.

### Americium Tetrafluoride

Table I summarizes the results of the several mass spectrometric (as well as the one supplemental) studies performed on americium tetrafluoride. After each of the high temperature experiments, a significant amount (comparable to the initial amount of sample) of solid residue remained inside of the cell. As with CeF₄(s), XRD analysis of a sample of AmF₄(s) heated to 800°C in a nickel container indicated that decomposition had occurred without any indication of significant fluorine effusion from the cell.

In an attempt to more completely passify the nickel cell prior to the decomposition study, nickel cells were fluorinated under the conditions used for the preparation of the MF₄(s) samples. When AmF₄(s) was heated in vacuum in these cells, F₂ was detected in the region of 600-700°C; XRD analysis of the residue of one of these samples confirmed that decomposition to AmF₃(s) had occurred. Subsequent heating of an empty fluorinated nickel cell in the experimental configuration yielded essentially the same F₂ signal in the same temperature region; apparently a nickel fluoride was decomposing although neither the decomposition of NiF₂(s) nor the existence of a higher nickel fluoride under these conditions are likely (9,10).

As both untreated nickel and fluorinated nickel were found to be unsuitable Knudsen cell materials for the study of AmF₄(s) decomposition, tantalum cells were tried. The ion fragments of the volatile TaF₅ species formed from the reaction of fluorine with the
cell were monitored with the mass spectrometer. In addition to an
experiment using a tantalum cell, one utilizing a sapphire cup to
contain the tetrafluoride sample within a tantalum cell was
performed (the latter configuration precluded the possibility of the
solid-solid reaction: \(5\text{AmF}_4(s) + \text{Ta}(s) \rightarrow 5\text{AmF}_3(s) + \text{TaF}_5(g)\)). In
both cases, the TaF\(_2\) fragment was monitored beginning at 400°C;
depletion of this signal occurred at 530°C and 600°C for the Ta and
Ta/Al\(_2\)O\(_3\) configurations, respectively.

In order to minimize the effect of containment interaction, a
mass spectrometric experiment was performed using a nickel cell
without any lid. With a direct line of sight from the americium
tetrafluoride sample to the ionization chamber, an F\(_2\) signal was
observed between 530 and 600°C.

A thermal treatment experiment was carried out in conjunction
with these mass spectrometric experiments. A submilligram sample of
AmF\(_4\)(s) was sealed under vacuum in a quartz capillary and analyzed
by XRD after each of several thermal treatments (each \(\approx 1 \text{ hr long}\)) at
intervals of \(\approx 50^\circ\) beginning at \(\approx 100^\circ\)C. Under these conditions,
americium tetrafluoride was found to decompose to AmF\(_3\)(s) at 300 ±
25°C. Because of the small sample size, relatively long heating
period, and possible reaction with SiO\(_2\), this temperature may not be
as accurate as those suggested by the other experiments reported
here but, at least, indicates decomposition at a lower temperature
than previously expected (4).

The mass spectrometric results obtained here indicate that
ameri2um tetrafluoride thermally decomposes in the region of 600°C.
This is in reasonable agreement with (6) and somewhat lower than
anticipated from the thermodynamic estimates of (4); however, more
recent predictions (\(\Delta H = 27 \text{ kcal/mol}\)) (1) are in better accord with
this decomposition behavior. It should be noted in this context
that although AmF\(_4\)(s) and CmF\(_4\)(s) may have similar decomposition
enthalpies (1,5), the difference between the expected 5f magnetic
entropy contributions to \(\Delta G\) is expected to result in a CmF\(_4\)(s)
decomposition temperature at least 200°C lower than that of AmF\(_4\)(s);
such has been observed to be the case (5).

Currently, other Knudsen cell materials (e.g., LaF\(_3\)) which will
allow complete and direct Knudsen effusion-mass spectrometric study
of the thermal decomposition of both AmF\(_4\)(s) and CeF\(_4\)(s) are being
investigated.

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REFERENCES


Table I. Results of Decomposition Studies of Cerium Tetrafluoride and Americium Tetrafluoride

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>CELL MATERIAL</th>
<th>RESULT</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>CeF₃⁺ to ~700°C</td>
</tr>
<tr>
<td>Cerium Tetrafluoride</td>
<td></td>
<td>CeF₃⁺ to ~700°C; CeF₄(s) $\xrightarrow{&lt;750°C}$ CeF₃(s)</td>
</tr>
<tr>
<td>I</td>
<td>Ni</td>
<td>CeF₃ to ~700°C</td>
</tr>
<tr>
<td>II</td>
<td>Ni</td>
<td>CeF₃⁺ to ~700°C</td>
</tr>
<tr>
<td>III</td>
<td>Ni</td>
<td>CeF₃⁺ to ~700°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CeF₄(s) $\xrightarrow{&lt;750°C}$ CeF₃(s)</td>
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<tr>
<td>Americium Tetrafluoride</td>
<td></td>
<td>AmF₄(s) $\xrightarrow{&lt;800°C}$ AmF₃(s)</td>
</tr>
<tr>
<td>I</td>
<td>Ni</td>
<td>TaF₂⁺, 400-530°C</td>
</tr>
<tr>
<td>II</td>
<td>Ta</td>
<td>TaF₂⁺, 400-530°C</td>
</tr>
<tr>
<td>III</td>
<td>Ni</td>
<td>TaF₂⁺, 400-530°C</td>
</tr>
<tr>
<td>IV</td>
<td>Ni-fluorinated</td>
<td>F₂ (from NiF₂); AmF₄(s) $\xrightarrow{&lt;700°C}$ AmF₃(s)</td>
</tr>
<tr>
<td>V</td>
<td>Ni-fluorinated</td>
<td>F₂⁺ (from NiF₂)</td>
</tr>
<tr>
<td>VI</td>
<td>Ni-no lid</td>
<td>F₂⁺, 530-690°C</td>
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<tr>
<td>VII</td>
<td>Al₂O₃/Ta</td>
<td>TaF₂⁺, 400-600°C; AmF₄(s) $\xrightarrow{&lt;650°C}$ AmF₃(s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AmF₄(s) $\xrightarrow{&lt;300°C}$ AmF₃(s)</td>
</tr>
</tbody>
</table>

a Description of cells in text.

b $I^+$ refers to shutterable ion signal observed by m.s. Reactions indicate results of XRD analysis of starting material and final product; temperature limits for these reactions indicate that decomposition occurred below this temperature. No F₂ detected unless otherwise specified.

c Results shown in Figure 1.