

THERMAL DECOMPOSITION OF LANTHANIDE AND ACTINIDE TETRAFLUORIDES

JOHN K. GIBSON and RICHARD G. HAIRE

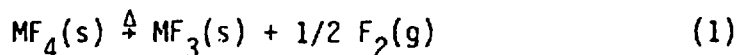
Chemistry Division, Oak Ridge National Laboratory  
Oak Ridge, Tennessee 37831-6375 U.S.A.

ABSTRACT

The thermal stabilities of several lanthanide/actinide tetrafluorides have been studied using mass spectrometry to monitor the gaseous decomposition products, and powder X-ray diffraction (XRD) to identify solid products. The tetrafluorides,  $TbF_4$ ,  $CmF_4$ , and  $AmF_4$ , have been found to thermally decompose to their respective solid trifluorides with accompanying release of fluorine, while cerium tetrafluoride has been found to be significantly more thermally stable and to congruently sublime as  $CeF_4$  prior to appreciable decomposition. The results of these studies are discussed in relation to other relevant experimental studies and the thermodynamics of the decomposition processes.

INTRODUCTION

Several of the lanthanide/actinide elements form both a solid trifluoride and a solid tetrafluoride. The relative stabilities of these fluorides may be studied through the thermal decomposition reaction:



This reaction is of particular interest as it provides a direct indication of the relative stabilities of the element's 3+ and 4+ oxidation states in the highly ionic environment provided by the crystalline fluorides:

$$\Delta H_{\text{decomp}}[\text{Eq. (1)}] = \Delta H_f[M^{III}F_3] - \Delta H_f[M^{IV}F_4]$$

We have recently undertaken to study Eq. (1) for  $MF_4 = CeF_4, TbF_4, AmF_4,$  and  $CmF_4$  [1,2]. The results of these studies are summarized and discussed in relation to the thermodynamics of Eq. (1) for these elements.

EXPERIMENTAL

The experimental details, including the preparation and characterization of the multimilligram-sized samples of the tetrafluorides, have been

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described previously [1,2]. The high temperature behavior of each of these compounds was studied by the Knudsen effusion - mass spectrometric technique. The gaseous decomposition ( $F_2(g)$ , monitored by the  $F_2^+$  ion-fragment) and/or sublimation ( $MF_4(g)$ , monitored by the  $MF_3^+$  ion-fragment) products released in vacuum from the condensed material in an effusion oven were monitored by a quadrupole mass spectrometer situated directly above the effusion orifice. In these particular studies the 300 amu upper mass limit of the quadrupole precluded direct study of  $AnF_4(g)$ -derived ions ( $An = Am$  or  $Cm$ ). The ion currents due to the samples were determined by the amount of attenuation of a particular mass ( $m/z$ ) peak upon insertion of a shutter between the Knudsen cell and the ionization chamber. The effusion cell was located in a resistance-heated furnace and the cell's temperature was measured with a chromel/alumel thermocouple in contact with it.

Careful selection of the container material for the high-temperature studies is particularly critical when highly reactive fluorine gas is generated, as by the reaction shown in Eq. (1). Our studies have shown that this reaction proceeds to completion below  $500^\circ C$  for  $TbF_4$  and  $CmF_4$ , and nickel cells are adequately resistant to  $F_2$  at these relatively low temperatures. However,  $AmF_4$  and  $CeF_4$  are stable above  $500^\circ C$  and it was found that nickel was not sufficiently passive and continuously reacted with fluorine at these higher temperatures. Although they are significantly more difficult to machine and handle, the use of lanthanum fluoride ( $LaF_3$ ) effusion cells avoided this problem for the study of  $AmF_4$  and  $CeF_4$ . The Knudsen cells were machined from rods of either high-purity Ni or  $LaF_3$  and had an internal volume of  $\sim 0.01 \text{ cm}^3$  and a cylindrical orifice diameter of 0.15 mm (Ni cells -  $TbF_4$  and  $CmF_4$ ) or 0.33 mm ( $LaF_3$  cells -  $CeF_4$  and  $AmF_4$ ). The cell bottom/orifice area ratios were 400 and 80, respectively. The larger orifice size and non-hermetic cell-lid seals in the  $LaF_3$  cells resulted in less than ideal equilibrium conditions for the  $CeF_4$  and  $AmF_4$  studies; the results of these experiments nonetheless provide a definitive indication of the nature and temperature regime of the dominant high-temperature decomposition or vaporization processes.

## RESULTS AND DISCUSSION

In Fig. 1 are plotted the mass spectrometric data obtained during two high-temperature studies of cerium tetrafluoride,  $CeF_4$ -I and  $CeF_4$ -II. Both  $F_2^+$  (38 amu) derived from  $F_2(g)$  (decomposition as given by Eq. (1)) and  $CeF_3^+$  (197 amu) arising from  $CeF_4(g)$  (congruent sublimation) were monitored above  $500^\circ C$ . The results are presented in the form of a van't Hoff plot,

$-\ln(I^+ \cdot T)$  vs  $T^{-1}$ , where  $I^+$  represents the measured current for the specified ion. Under equilibrium conditions,  $P_i = k_i \cdot I^+ \cdot T$ , and the data so plotted should fall on a straight line with slope describing the enthalpy of the decomposition or vaporization process producing the parent vapor species [3]. As discussed above, and reflected in the nonlinearity of even the lowest-temperature data in Fig. 1, it is likely that true equilibrium conditions were not obtained inside of the  $\text{LaF}_3$  cells. The sharp drop in both the  $\text{F}_2^+$  and the  $\text{CeF}_3^+$  ion-fragment signals in the region of  $800^\circ\text{C}$  indicated depletion of the  $\text{CeF}_4$  samples by congruent sublimation and/or by decomposition to non-volatile  $\text{CeF}_3$ . Visual examination of the interior of the effusion cells after these measurements revealed essentially no solid residue, indicating sublimation as the primary high-temperature process. Thus, although a small  $\text{F}_2$  (as  $\text{F}_2^+$ ) signal was detected during the experiments, it can be concluded that  $\text{CeF}_4$  did not appreciably decompose according to Eq. (1) until temperatures above  $\sim 800^\circ\text{C}$  were reached. This conclusion is in accord with the observation of substantial tetrafluoride stability of Asker and Wylie [4] but in contrast to the results of several other studies [5 and references therein].

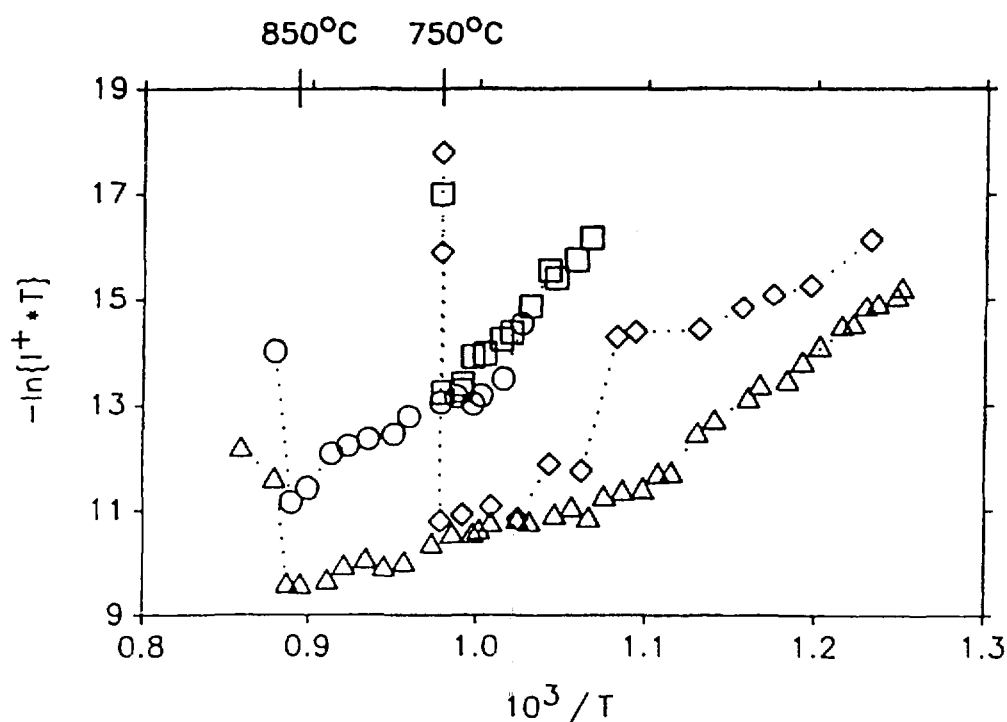


Fig. 1 - Results of mass spec. studies of  $\text{CeF}_4$ :  $\Delta = \text{CeF}_3^+/\text{CeF}_4\text{-I}$ ;  $\circ = \text{F}_2^+/\text{CeF}_4\text{-I}$ ;  $\diamond = \text{CeF}_3^+/\text{CeF}_4\text{-II}$ ;  $\square = \text{F}_2^+/\text{CeF}_4\text{-II}$ .

The results of the high-temperature studies of  $\text{CmF}_4$  and  $\text{TbF}_4$  are shown in Fig. 2 in the form of van't Hoff plots. In each case,  $F_2^+$  measurements were made from  $300^\circ\text{C}$  until the sample depleted, at  $\sim 450^\circ\text{C}$  for  $\text{CmF}_4$  or  $\sim 500^\circ\text{C}$  for  $\text{TbF}_4$ . A solid residue estimated visually as comparable in amount to that of the starting tetrafluorides was found at the end of each experiment, and was identified by XRD as the corresponding trifluoride. The linearity of the data in Fig. 2 prior to depletion of the sample is in accord with predictions of vapor saturation in these particular effusion cells; the indicated linear fits to the data give decomposition enthalpies (for Eq. (1)) of 26 and 24 kcal/mole for  $\text{CmF}_4$  and  $\text{TbF}_4$ , respectively. This latter value is in reasonable accord with a previous study of  $\text{TbF}_4$  [6] where a decomposition enthalpy of 19 kcal/mole was determined; an experimental value for  $\text{CmF}_4$  was not previously reported.

The results of similar studies of two  $\text{AmF}_4$  samples are shown in Fig. 3. As with the  $\text{CeF}_4$  experiments, these results may reflect non-saturated vapor conditions in the  $\text{LaF}_3$  effusion cells, and therefore a Second Law treatment of the data was not performed. The large drop in the  $F_2^+$  ion-currents in Fig. 3 at  $\sim 700^\circ\text{C}$  signals depletion of the  $\text{AmF}_4$  samples. X-ray diffraction analysis of the substantial solid residues in these cells identified them as

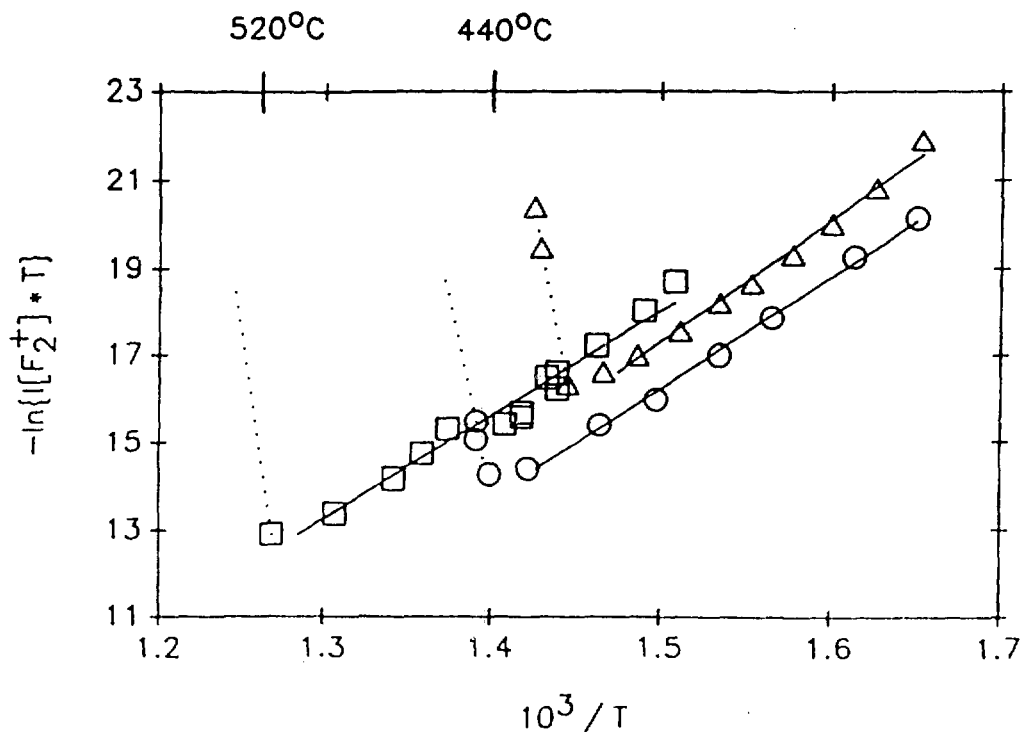
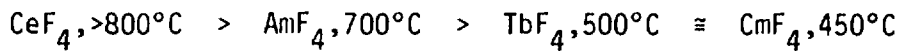


Fig. 2 - Results of mass spec. studies of  $\text{CmF}_4$  and  $\text{TbF}_4$ :  $\bigcirc = F_2^+/\text{CmF}_4$ -I;  $\triangle = F_2^+/\text{CmF}_4$ -II;  $\square = F_2^+/\text{TbF}_4$ -I.

$\text{AmF}_3$ , indicating that thermal decomposition, Eq. (1), occurred prior to appreciable sublimation. Although thermodynamic considerations [7] have predicted a greater thermal stability than implied by this result, it is in accord with indirect experimental evidence for the thermal decomposition of  $\text{AmF}_4$  obtained by Chudinov and Choporov [8].

In summary, we have established the following order (and approximate thermal decomposition/depletion temperatures) for the thermal stabilities of the solid tetrafluorides studied:



The decomposition enthalpies cited in ref. [1] are in qualitative accord with this ordering, but decomposition entropies must be estimated to derive decomposition free energies for quantitative thermodynamic comparisons for Eq. (1). Except for the  $5f^n$  magnetic contribution from the lanthanide/actinide species, the entropies associated with Eq. 1 for different metals should be very similar. The following magnetic contributions to the decomposition entropies,  $\Delta S_{d/m}$ , may be estimated using the approach of Ward and Hill [9]:  $\text{CeF}_4$ , 3.6 e.u.;  $\text{AmF}_4$ , -3.6 e.u.;  $\text{TbF}_4$ , 1.0 e.u.;  $\text{CmF}_4$ , 4.1 e.u. Using the decomposition enthalpies,  $\Delta H_d[\text{MF}_4]$ , from [1] ( $\text{CeF}_4$ , 58

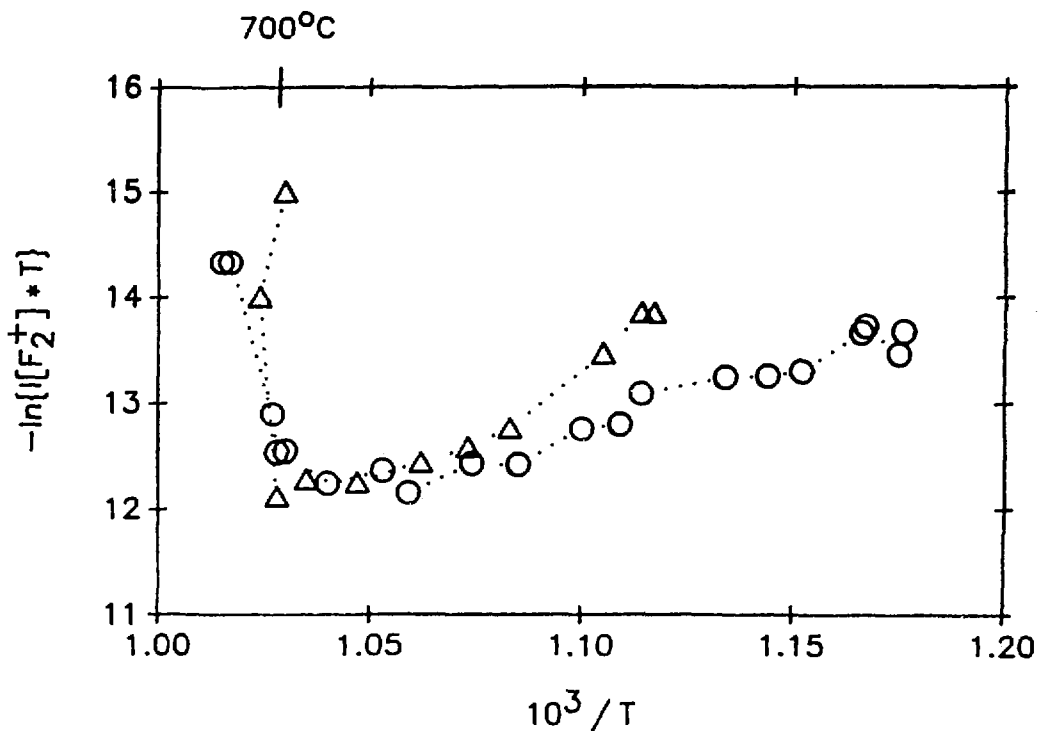


Fig. 3 - Results of mass spec. studies of  $\text{AmF}_4$ :  $\text{O} = \text{F}_2^+/\text{AmF}_4\text{-I}$ ;  
 $\Delta = \text{F}_2^+/\text{AmF}_4\text{-II}$ .

kcal/mole;  $\text{AmF}_4$ , 27 kcal/mole;  $\text{TbF}_4$ , 20 kcal/mole;  $\text{CmF}_4$ , 26 kcal/mole) and taking the nonmagnetic contributions to the decomposition entropies to be the same as that for  $\text{PuF}_4$  ( $\Delta S_{d/\text{non-mag}}[\text{PuF}_4] = 20$  e.u. [7]), the following free energies of decomposition,  $\Delta G_d[\text{MF}_4] = \Delta H_d - T\Delta S_d$ , are derived (at  $T = 1000$  K):

$$\text{CeF}_4, 34 \text{ kcal/mole} > \text{AmF}_4, 11 > \text{TbF}_4, -1 \approx \text{CmF}_4, 2$$

It is seen that this comparison of estimated thermodynamic stabilities is in good agreement with the decomposition temperatures observed in this study.

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