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THERMAL DECOMPOSITION OF LANTHANIDE AND ACTINIDE TETRAFLUORIDES

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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:

$$MF_4(s) \xrightarrow{\Delta} MF_3(s) + 1/2\ F_2(g) \qquad (1)$$

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:

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

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°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°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 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°C. The results are presented in the form of a van't Hoff plot,

$-\ln(I^{+}.T)$ vs T^{-1}, where I^{+} represents the measured current for the specified ion. Under equilibrium conditions, $P_i = k_i.I^{+}.T$, 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 LaF_3 cells. The sharp drop in both the F_2^+ and the CeF_3^+ ion-fragment signals in the region of 800°C indicated depletion of the CeF_4 samples by congruent sublimation and/or by decomposition to non-volatile 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 F_2 (as F_2^+) signal was detected during the experiments, it can be concluded that CeF_4 did not appreciably decompose according to Eq. (1) until temperatures above ~800°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].

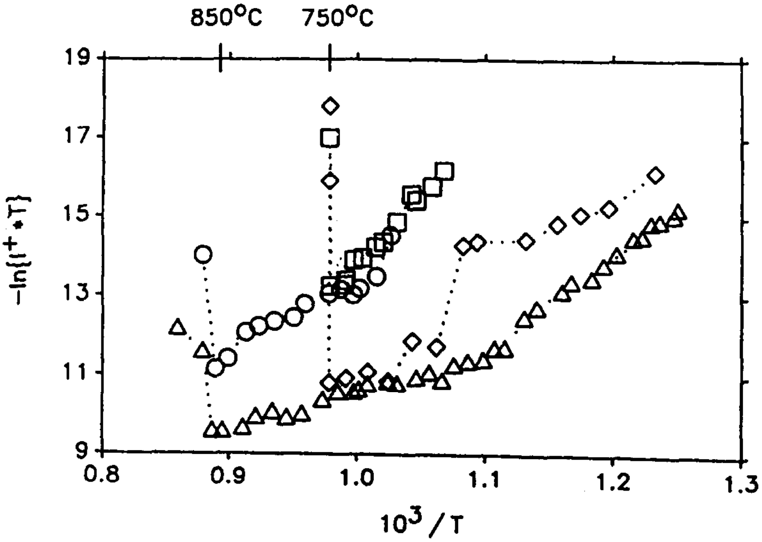

Fig. 1 - Results of mass spec. studies of CeF_4: △ = CeF_3^+/CeF_4-I; ○ = F_2^+/CeF_4-I; ◇ = CeF_3^+/CeF_4-II; □ = F_2^+/CeF_4-II.

The results of the high-temperature studies of CmF_4 and 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°C until the sample depleted, at ∿450°C for CmF_4 or ∿500°C for 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 CmF_4 and TbF_4, respectively. This latter value is in reasonable accord with a previous study of TbF_4 [6] where a decomposition enthalpy of 19 kcal/mole was determined; an experimental value for CmF_4 was not previously reported.

The results of similar studies of two AmF_4 samples are shown in Fig. 3. As with the CeF_4 experiments, these results may reflect non-saturated vapor conditions in the 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 ∿700°C signals depletion of the AmF_4 samples. X-ray diffraction analysis of the substantial solid residues in these cells identified them as

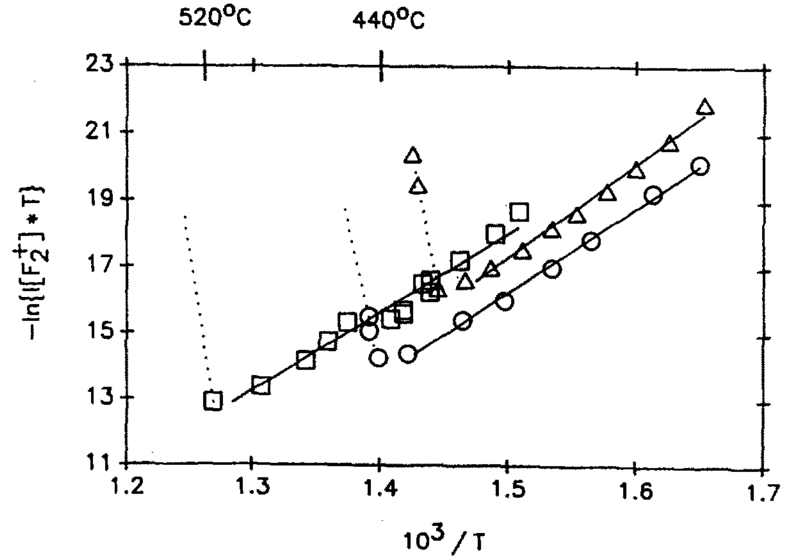

Fig. 2 - Results of mass spec. studies of CmF_4 and TbF_4: ○ = F_2^+/CmF_4-I; △ = F_2^+/CmF_4-II; □ = F_2^+/TbF_4-I.

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 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:

CeF_4,>800°C > AmF_4,700°C > TbF_4,500°C ≅ CmF_4,450°C

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]: CeF_4, 3.6 e.u.; AmF_4, -3.6 e.u.; TbF_4, 1.0 e.u.; CmF_4, 4.1 e.u. Using the decomposition enthalpies, $\Delta H_d[MF_4]$, from [1] (CeF_4,58

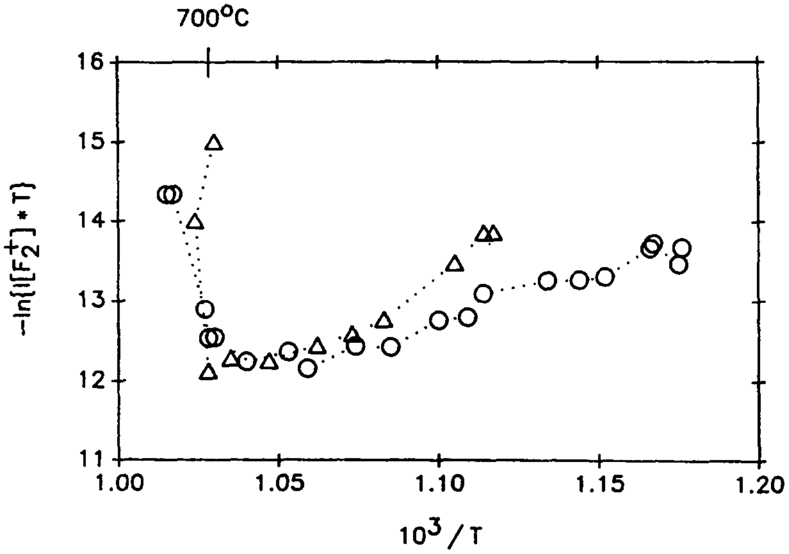

Fig. 3 - Results of mass spec. studies of AmF_4: ○ = F_2^+/AmF_4-I; △ = F_2^+/AmF_4-II.

kcal/mole; AmF_4,27 kcal/mole; TbF_4,20 kcal/mole; CmF_4,26 kcal/mole) and taking the nonmagnetic contributions to the decomposition entropies to be the same as that for PuF_4 ($\Delta S_{d/non-mag}[PuF_4]$ = 20 e.u. [7]), the following free energies of decomposition, $\Delta G_d[MF_4] = \Delta H_d - T\Delta S_d$, are derived (at T = 1000 K):

$$CeF_4,34 \text{ kcal/mole} > AmF_4,11 > TbF_4,-1 \cong CmF_4,2$$

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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