THERMAL STABILITIES OF AMERICIUM AND CERIUM TETRAFLUORIDES

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Summary

The thermal stabilities of americium and cerium tetrafluorides were determined by mass spectrometry, monitoring their gaseous vaporization and/or decomposition products as a function of temperature. For americium tetrafluoride, the dominant high temperature (less than or equal to 700 °C) process is thermal decomposition to the trifluoride

$$\operatorname{AmF}_4(s) \xrightarrow{\Delta} \operatorname{AmF}_3(s) + \frac{1}{2} \operatorname{F}_2(g)$$

In contrast, with cerium tetrafluoride, the most prominent process at high temperature (less than or equal to 850 $^{\circ}$ C) is congruent sublimation

$$\operatorname{CeF}_4(s) \xrightarrow{\Delta} \operatorname{CeF}_4(g)$$

The results of these studies are interpreted in terms of the relevant thermodynamic parameters for each process and are compared with predictions and results which have been reported in the literature.

1. Introduction

For those lanthanide or actinide elements which form both a solid tetrafluoride and trifluoride, the thermal decomposition process shown in eqn. (1) provides an indication of the relative stabilities of the tetravalent and trivalent states.

$$M^{IV}F_4(s) \xrightarrow{\Delta} M^{III}F_3(s) + \frac{1}{2}F_2(g)$$
 (1)

In addition to this decomposition process, the tetrafluorides, if sufficiently stable, may sublime congruently

$$MF_4(s) \xrightarrow{\Delta} MF_4(g)$$
 (2)

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As discussed in ref. 1, thermodynamic predictions that PrF_4 , TbF_4 and CmF_4 decompose below 500 °C have been confirmed experimentally. In contrast, UF_4 , NpF_4 and PuF_4 are substantially more stable and sublime congruently prior to appreciable thermal decomposition [2]. Cerium tetrafluoride would be expected to have a thermodynamic stability comparable with that of PuF_4 , yet several studies [3 - 7] have suggested that CeF_4 decomposes below 400 °C according to eqn. (1). A study by Asker and Wylie [8] established that pure CeF_4 is thermally stable to approximately 800 °C, and that it is the hydrated and ammoniated materials ($CeF_4 \cdot H_2O$; $CeF_4 \cdot \frac{1}{2}NH_4F$) which decompose to CeF_3 below 500 °C. Subsequent investigations [9, 10] have confirmed the thermal stability of pure CeF_4 up to at least 800 °C.

Estimates of the thermodynamic quantities associated with the thermal decomposition of AmF_4 have suggested that its thermal stability is between those of CmF_4 and CeF_4 [2, 11]. Given the contrasting high temperature behavior for these two compounds (decomposition for CmF_4 compared with sublimation for CeF_4), it was the intent of this work to establish the high temperature behavior of AmF_4 . The only high temperature study of AmF_4 reported previously involved the determination of the vapor pressure of the tetrafluoride from mass transfer experiments [12]. Irregularities in the results at the higher temperatures (greater than 660 °C) were interpreted as indirect evidence for appreciable thermal decomposition of AmF_4 (eqn. (1)).

We have undertaken to establish the relative importance of the two high temperature processes (decomposition in eqn. (1) and sublimation in eqn. (2)) for AmF_4 , and have also carried out a comparable study of the high temperature behavior of CeF_4 . Mass spectrometry was used to monitor the volatile products generated at high temperature, and X-ray diffraction analysis was used to identify solid products remaining after the high temperature treatment. By selecting LaF_3 as the cell material for the tetrafluoride samples, it was possible to minimize the high temperature fluorine corrosion encountered in previous attempts with metal cells [13].

2. Experimental details

2.1. Tetrafluoride preparation and analysis

The ²⁴³Am 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; the ²⁴³Am isotope ($t_{1/2} = 7370$ years, α decay) accounted for more than 99.98% of the americium. Spark source mass spectrographic analysis of portions of the americium used for this work indicated a total metallic impurity level of less than 200 wt. ppm. Cerium tetrafluoride was prepared from 99.9% CeCl₃.

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 programmed temperature cycles up to 450 $^{\circ}$ C. The

trifluorides had been prepared by aqueous precipitation with HF, followed by drying at 110 °C. Further details of the preparative technique are given in ref. 14. All of the starting materials, as well as the residues resulting from high temperature decompositions, were analyzed by conventional X-ray diffraction (XRD) using Mo K α radiation and Debye–Scherrer powder cameras (diameter, 114.6 mm).

2.2. Fluoride containment and mass spectroscopy

It was established previously that nickel cells react with the fluorine generated during the decomposition of the tetrafluorides at the temperatures necessary for the appreciable vaporization and/or decomposition of AmF_4 and CeF_4 [13]. To avoid this complication, lanthanum fluoride (LaF₃) was selected as the cell material for these studies; LaF₃ is chemically inert under these experimental conditions and does not have a significant vapor pressure below 1000 °C.

Two Knudsen cells were machined from a high purity, optical grade LaF_3 rod of 5 mm diameter. The cells had a cylindrical orifice diameter of 0.33 mm (with $L/r \approx 2$) and an internal volume of approximately 0.01 cm³. The ratio of the cell's bottom area (approximately equal to sample surface) to the orifice area was approximately 80. With the LaF_3 cells, in contrast with metal cells of the same design, it was not possible to obtain a completely hermetic seal between the cell body and lid. Owing to the limited availability of these LaF_3 cells, it was necessary to reuse them for some experiments, after they had been emptied of all solid residue.

For each experiment, approximately 5 mg of americium tetrafluoride or approximately 10 mg of cerium tetrafluoride was placed into the cell. To minimize exposure of the samples to air and moisture, most handling of the tetrafluorides was carried out in a helium-filled glove-box. Some minimal atmospheric exposure was unavoidable during the loading of the cell into the mass spectrometer system, which was located in an air-filled α -containment glove-box. The mass spectrometer system and the experimental procedures for the vaporization studies have been described in ref. 1. All of the vaporization experiments were performed with a background pressure below $1 \times$ 10^{-6} Torr. Calibration of the temperature measurements (type-K thermocouple) was accomplished by observation of the melting points of high purity gold (1064 °C) and lanthanum (921 °C) metals contained in an open (no lid) tantalum cell in the normal experimental configuration. With both metals, the observed melting points were within 10 $^{\circ}$ C of the accepted values; temperature corrections were not applied to the measured temperatures and the values reported here are considered to be accurate to ± 15 °C.

An ionizing electron energy of 70 eV was used throughout the experiments. The ion intensities reported here correspond to the net shutterable current for a particular m/z peak, obtained from intensities before and after insertion of a shutter between the Knudsen cell orifice and the mass spectrometer ionization chamber. The determination of various effects additional to those reported (e.g. thermal hysteresis, ionization efficiencies, minor MF_{4-x}^+ ion fragment intensities, etc.) was precluded by the relatively small sample sizes. These were required because of the microscale nature of this system, which is designed to allow the study of the highly radioactive transplutonium elements.

3. Results and discussion

3.1. High temperature behavior of cerium tetrafluoride

High temperature studies were carried out on cerium tetrafluoride samples prepared in our laboratory. Powder XRD patterns obtained for this cerium fluoride indicated it to be CeF_4 , with the ZrF_4 -type monoclinic crystal structure [15].

Two high temperature vaporization experiments were performed using the prepared monoclinic CeF_4 and they are denoted respectively as CeF_4 -A and CeF_4 -B. Experiment CeF_4 -A was performed with an LaF_3 Knudsen cell used previously for high temperature studies of AmF_4 (the two experiments AmF_4 -A and AmF_4 -B); experiment CeF_4 -B was performed with a pristine LaF_3 cell.

In each CeF_4 study, the two most intense (shutterable) ion peaks measured were attributed to CeF_3^+ (197 a.m.u.) and F_2^+ (38 a.m.u.). The assignment of the 197 a.m.u. peak was substantiated by observation of a corresponding peak at 199 a.m.u. with a relative intensity in accord with the ¹⁴⁰Ce:¹⁴²Ce isotopic abundance ratio of 8:1. The CeF₃⁺ ion is the most abundant fragment generated by the ionization of gaseous CeF4 under our experimental conditions [9]. The measured F_2^+ and CeF_3^+ ion intensities are shown in Fig. 1 as a plot of $-\ln(I^+T)$ vs. T^{-1} . For these measurements, the electron multiplier high voltage (gain) was greater for CeF_4 -A than for CeF_4 -B. (With the exception of the CeF_4 -B sample, all ion intensity measurements were made with the same instrument parameters as used for CeF₄-A.) Under equilibrium (vapor saturation) conditions in the Knudsen flow regime, the equality $P_i = k_i I_i^{+} T$ should hold and, according to the van't Hoff relation, plots of the mass spectral data as a function of temperature should fall on a straight line, the slope of which represents the enthalpy for the vaporization or decomposition process. This can be represented by the following relations [16].

$$\frac{1}{2} \operatorname{d} \ln \{I(\mathbf{F}_2^+) \times T\} / \operatorname{d}(1/T) = -\Delta H_{\mathrm{d}}(\operatorname{CeF}_4) / R$$

and sublimation

 $d \ln \{I(\text{CeF}_4^+) \times T\}/d(1/T) = -\Delta H_s(\text{CeF}_4)/R$

The linear fit to the low temperature (530 - 670 °C) CeF_3^+ data for sample CeF_4 -A is indicated in Fig. 1 (top) and gives $\Delta H_s(\text{CeF}_4) = 50$ kcal mol⁻¹.



Fig. 1. Results of vaporization-decomposition studies of monoclinic CeF₄: \bigcirc , F₂⁺ (38 a.m.u.); \triangle , CeF₃⁺ (197 a.m.u.). Top, CeF₄-A; depletion of mass spectral signals occurs at approximately 850 °C; linear fit to low temperature CeF₃⁺ data gives $\Delta H_{\rm s}$ (CeF₄) = 50 kcal mol⁻¹. Bottom, CeF₄-B; depletion of mass spectral signals occurs at approximately 750 °C.

This value is somewhat lower than the $66 \pm 4 \text{ kcal mol}^{-1}$ (at 700 °C) measured by Badtiev *et al.* [10], and in our work it may reflect the depression of the apparent CeF₄ pressure to below equilibrium values with increasing temperatures, an effect which became pronounced at higher temperatures. The F₂⁺ (F₂(g); decomposition) and CeF₃⁺ (CeF₄(g); sublimation) ion signals above 700 °C were clearly depressed below the extrapolated equilibrium values in both the CeF₄-A and CeF₄-B studies. An acute drop in both the F₂⁺ and CeF₃⁺ intensities was observed at 850 °C for CeF₄-A and at 750 °C for CeF₄-B. The difference of approximately 100 °C between the observed sample depletion temperatures for these two CeF₄ experiments may be due to differences in the masses of the samples, differences in the thermal histories (time at temperature) and/or differences in the degree of vapor leakage through the cell-lid seals. The slopes of the F₂⁺ data were not used to derive Second Law decomposition enthalpies because of the clearly non-equilibrium behavior of the samples; in accord with the effect of depletion, slopes

suggested by the F_2^+ data shown in Fig. 1 are significantly smaller than expected from the thermodynamic stabilities of CeF₄ and CeF₃ [10, 11].

Visual examination of the cells after these experiments revealed no detectable solid residue remaining therein. Since the vapor pressure of $CeF_3(s)$ is essentially negligible below 1000 °C [16], this observation alone implies that virtually all of the cerium tetrafluoride sublimed congruently as $CeF_4(g)$ without decomposition to $CeF_3(s)$. Such an interpretation is also consistent with the depletion behavior demonstrated by the data in Fig. 1. It is also apparent from Fig. 1 that the F_2^+ signals are smaller than the isothermal $\operatorname{CeF_3}^+$ signals. The relative pressures of $F_2(g)$ and $\operatorname{CeF_4}(g)$ over solid cerium tetrafluoride may be estimated from the low temperature (conditions best representing equilibrium) F_2^+ and CeF_3^+ ion intensity data using the following approximations: (i) the electron multiplier gain is independent of mass [17]; (ii) the ionization cross-section of CeF₄ is 10 times that of F_2 [18, 19]; and (iii) the quadrupole transmission efficiency of F_2^+ (38 a.m.u.) is 10 times that of CeF_3^+ (197 a.m.u.) [20]. The result of this estimate is that $P(\text{CeF}_4)/P(\text{F}_2) = \{k(\text{CeF}_3^+)/k(\text{F}_2^+)\}\{I(\text{CeF}_3^+)/I(\text{F}_2^+)\} \approx 10.$ This value supports the conclusion that the primary high temperature process is the congruent sublimation of CeF_4 .

3.2. High temperature behavior of americium tetrafluoride

The americium tetrafluoride preparation was analyzed by powder XRD and was found to be AmF_4 with the ZrF_4 -type monoclinic crystal structure [21]. Two vaporization experiments were performed with this material and are denoted as AmF_4 -A and AmF_4 -B. Experiment AmF_4 -A was carried out with a pristine LaF_3 cell, whereas sample AmF_4 -B was studied in the cell previously used for AmF_4 -A.

An F_2^+ signal was measured between 580 and 710 °C for AmF_4 -A and between 620 and 700 °C for AmF_4 -B; in each case, acute depletion of the F_2^+ signal occurred at approximately 700 °C. The F_2^+ measurements are shown as Arrhenius-type plots in Fig. 2. As in the case of the CeF₄ results, Second Law enthalpies of decomposition were not derived from these data owing to the pressure-depressing influence of accelerating sample depletion with increasing temperature. As with the F_2^+ -CeF₄ data (Fig. 1), the approximate slopes suggested by the F_2^+ -AmF₄ data (Fig. 2) are significantly smaller than expected from thermodynamic considerations [2, 11]; a smaller apparent Second Law decomposition or vaporization enthalpy would be the predicted effect of sample depletion. Because of the limited useful upper mass limit (300 a.m.u. ideal maximum) of the quadrupole used for these experiments, the ion fragments which would have resulted from the congruent sublimation of americium tetrafluoride could not be monitored.

Visual examination of the cells at the end of each AmF_4 high temperature experiment revealed a solid present in an amount comparable with that of the starting material. XRD analyses of these residues showed them to be AmF_3 with the LaF₃-type trigonal crystal structure [22]. Thus the dominant high temperature process for americium tetrafluoride is the decomposition



Fig. 2. Results of decomposition studies of monoclinic AmF_4 : \circ , F_2^+ (38 a.m.u.). Top, AmF_4 -A; bottom, AmF_4 -B; depletion of F_2^+ signals for both samples occurs at approximately 700 °C.

to americium trifluoride with the accompanying generation of fluorine (eqn. (1)). This conclusion is in accord with the indirect results of Chudinov and Choporov [12], who interpreted sub-equilibrium $AmF_4(g)$ pressure above 660 °C reflecting thermal decomposition of the $AmF_4(s)$ source.

Experiments AmF_4 -A, AmF_4 -B and CeF_4 -A were performed with similar geometries and measurement parameters, and their F_2^+ intensity values may thus be compared directly. To the extent that these measured F_2^+ intensity values represent equilibrium decomposition fluorine pressures, it may be concluded that the fluorine pressure over AmF_4 was at least 10 times greater than that over CeF_4 ; this comparison is also consistent with the conclusion that eqn. (1) (decomposition) is dominant in the case of AmF_4 , whereas eqn. (2) (sublimation) dominates in the case of CeF_4 .

4. Conclusions

It was established that $CeF_4(s)$ sublimes congruently without appreciable thermal decomposition to $CeF_3(s)$. This finding is in accord with

reports of certain other investigators [8 - 10], but contrasts the results

reported in several other cases [3 - 7]. As suggested by the work of Asker and Wylie [8], it appears likely that these latter investigations utilized solvated or otherwise impure fluoride samples.

In contrast with the behavior of cerium tetrafluoride, we established that $AmF_4(s)$ thermally decomposes in vacuum to $AmF_3(s)$. Although some congruent sublimation must occur concurrently [12], it was concluded that thermal decomposition is the dominant high temperature vaporization mechanism for americium tetrafluoride. Our finding that AmF_4 thermally decomposes more readily than CeF_4 is consistent with disproportionation enthalpies predicted using the bonding model of Brooks *et al.* [23].

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