

## VAPORIZATION STUDIES OF MIXED LANTHANIDE TRIFLUORIDES

JOHN K. GIBSON and RICHARD G. HAIRE

*Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6375 (U.S.A.)*

(Received 29 September 1987; in final form 10 November 1987)

### ABSTRACT

A Knudsen effusion–mass spectrometry technique has been used to simultaneously study the congruent high-temperature ( $\sim 1500$  K) vaporization of each component from the mixed lanthanide trifluoride systems (1)  $\text{HoF}_3 + \text{TmF}_3$ ; (2)  $\text{TbF}_3 + \text{HoF}_3 + \text{LuF}_3$ ; (3)  $\text{LaF}_3 + \text{GdF}_3 + \text{LuF}_3$ ; and (4)  $\text{LaF}_3 + \text{PrF}_3 + \text{HoF}_3 + \text{LuF}_3$ . Such investigations provide relative vapor pressures and enthalpies of vaporization for each of the 2–4 components of the mixture that are more reliable than those derived from independent experiments with a single fluoride. The trend in the trifluoride vaporization thermodynamics across the lanthanide series derived from the present investigation is in better accord with comparable systematics for the other lanthanide trihalides, and more regular in nature than was suggested by data from previous studies.

### INTRODUCTION

Enthalpies of sublimation/vaporization for the lanthanide trifluorides ( $\text{LnF}_3$ ) are approximately  $100 \text{ kcal mol}^{-1}$ , and the variation in this quantity across the lanthanide series is expected to be less than 10% of this value. Establishing the systematics of  $\text{LnF}_3$  vaporization thermodynamics thus requires more accurate determinations of relative vapor pressures/enthalpies of vaporization than often result from typical high temperature experiments utilizing the individual fluorides. Values for  $\Delta H_{\text{subl},298 \text{ K}}(\text{LnF}_3)$  suggested in a critical review by Myers and Graves of experimental work [1], for example, indicate unexpected irregularities in the trend across the lanthanide series. As noted by these authors [1], and illustrated by their values (plotted in Fig. 1), the uncertainty associated with each lanthanide trihalide sublimation enthalpy is too great to allow meaningful conclusions to be drawn regarding systematics. An interpretation of deviations from monotonic regularity, such as suggested by the graphs for  $\text{LnF}_3$  (and  $\text{LnCl}_3$ ) in Fig. 1 would be of interest if these irregularities are indeed real. However, it was considered desirable to first confirm the lanthanide trifluoride vaporization systematics with more accurate relative measurements as used in this work.

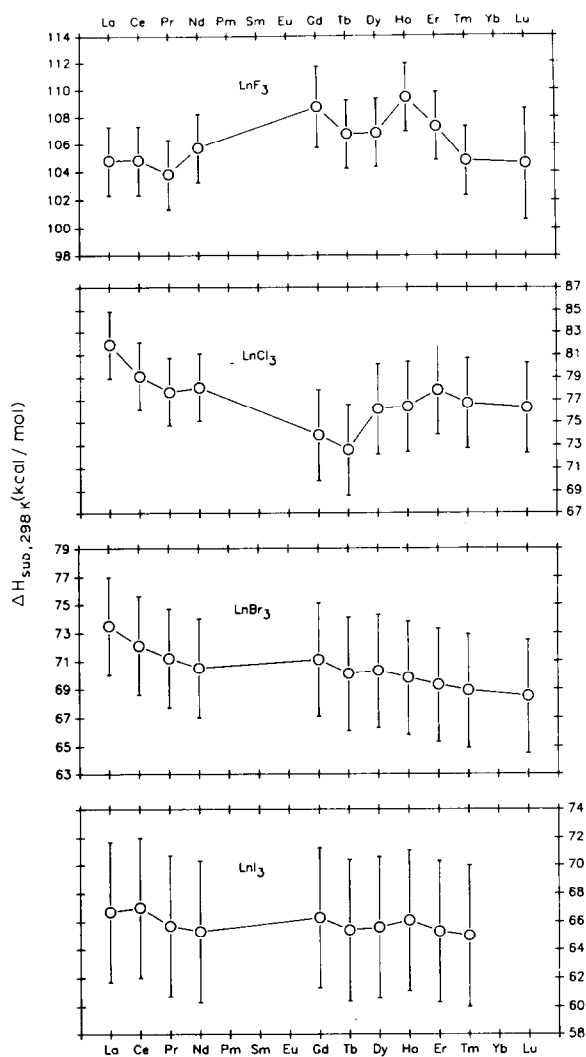


Fig. 1. Sublimation enthalpies of lanthanide trihalides [1].

Many of the uncertainties associated with high-temperature vaporization studies derive from systematic (and random) errors in temperature measurement/gradients, materials interactions, non-ideal effusion conditions, mass spectrometer calibrations, etc. A simultaneous study of the vaporization of two or more components of a mixture can provide more accurate determinations of relative thermodynamic quantities due to the cancellation of various sources of error. This approach has been used here to derive relative vapor pressures and enthalpies of vaporization using mixtures of two or more lanthanide trifluorides. Results are reported here for a Knudsen effusion-mass spectrometric investigation of the high temperature vaporization of the components in the systems (1)  $\text{HoF}_3 + \text{TmF}_3$ ; (2)  $\text{TbF}_3 + \text{HoF}_3 +$

$\text{LuF}_3$ ; (3)  $\text{LaF}_3 + \text{GdF}_3 + \text{LuF}_3$ ; and (4)  $\text{LaF}_3 + \text{PrF}_3 + \text{HoF}_3 + \text{LuF}_3$ . Interpretations of the results, including consideration of additional factors which may affect vaporization from such mixtures, are discussed.

## EXPERIMENTAL

All fluorides used in this work were commercial powders (99.9%, -325 to -60 mesh). Powder X-ray diffraction analysis of the starting fluorides performed by the supplier (Cerac) indicated the following crystal symmetries: hexagonal  $\text{LaF}_3$ ,  $\text{PrF}_3$ ; orthorhombic  $\text{GdF}_3$ ,  $\text{TbF}_3$ ,  $\text{HoF}_3$ ,  $\text{TmF}_3$ , and  $\text{LuF}_3$ . The fluoride samples were prepared by mechanically mixing weighed portions (2-4 mg of each, weighed to  $\pm 0.1$  mg) prior to loading into the Knudsen cell. The net composition of each mixture was such that the lanthanide contents were within 35% of each other.

The tantalum Knudsen cells had an internal volume of  $\sim 0.01$  cm<sup>3</sup>, an orifice area of  $\sim 2 \times 10^{-4}$  cm<sup>2</sup>, and a length/diameter ratio of  $\sim 2$ . A tantalum sheath separated the cell from a tantalum coil resistance heater and served to homogenize the temperature in the region of the cell. During the experiments, the cell rested on a nickel disk, into the bottom of which chromel and alumel wires were welded to form an intrinsic type-K thermocouple. Temperature calibration was by observation of the melting point of gold metal (m.p. = 1065°C) contained in an open tantalum cell placed in the experimental configuration. Two independent calibrations indicated thermocouple readings 30°C high. The corrected temperatures used here are considered accurate to  $\pm 20$ °C (absolute uncertainty; uncertainties in relative temperatures are significantly smaller).

The ionization chamber of a UTi 100C 1-300 amu quadrupole mass spectrometer was positioned 7 cm above the cell orifice. The high-vacuum chamber was maintained below  $10^{-6}$  torr during the high temperature measurements by a turbomolecular pumping system. Electrons with an energy of 70 eV were used to ionize/fragment the Knudsen cell effusate. The mass-filtered ions were detected and their intensities amplified with a Channeltron electron multiplier; the mass spectra were recorded on a strip chart recorder. Use of an externally operated shutter located between the cell and ionization chamber allowed that portion of each mass peak which derived from the cell to be identified. Mass signal intensities reported here refer to the shutterable portion of the measured peaks.

## RESULTS AND DISCUSSION

For each fluoride mixture, mass spectral signals associated with the congruent vaporization of each of the  $\text{LnF}_3$  components were measured over

some portion of the range 900–1250 °C. Significant curvature is not apparent in van 't Hoff plots of the data ( $\ln(I^+ \cdot T)$  vs.  $1/T$ ), suggesting that appreciable composition changes (selective depletion) did not occur up to the highest temperatures attained in the experiments. This is consistent with material loss rates of  $< 10 \mu\text{g min}^{-1}$  calculated from the vapor pressures ( $< 0.05$  torr at 1270 °C) reported for several lanthanide trifluorides by Zmbov and Margrave [2].

Although the dominant  $\text{LnF}_2^+$  ( $\sim 90\%$ ) fragment ion was used to monitor the  $\text{LnF}_3$  vapor species, the  $\text{LnF}^+$  ( $\leq 10\%$ ),  $\text{Ln}^+$  ( $\leq 10\%$ ), and (in some instances)  $\text{LnF}_3^+$  (usually  $< 10\%$ ) peaks were also identified. In the cases of  $\text{PrF}_3$ - and  $\text{TbF}_3$ -containing mixtures, their  $\text{LnF}_3^+$  ion peaks were significantly more intense than were the  $\text{LnF}_3^+$  peaks of the other lanthanide trifluorides — this behavior may reflect the relatively high stability of  $\text{TbF}_4$  and  $\text{PrF}_4$ , although the source of fluorine for oxidation to the tetravalent state is unknown. In addition, peaks considered to derive from the  $\text{TaF}_5$  vapor species (especially  $\text{TaF}^+$  and  $\text{TaF}_2^+$  at 200 and 219 amu, respectively) were identified, and presumably originated from the tantalum components in the experimental apparatus.

A (2.5 min) mass scan taken during the  $\text{LaF}_3 + \text{PrF}_3 + \text{HoF}_3 + \text{LuF}_3$  experiment is shown in Fig. 2; this plot is typical for the data obtained in

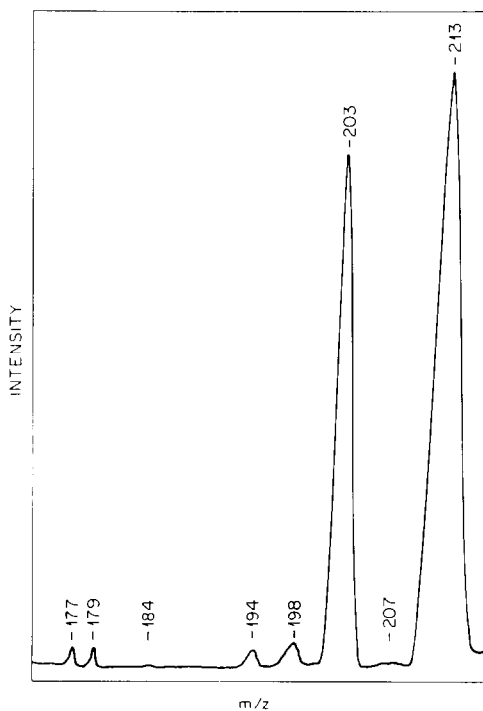


Fig. 2. Mass spectrum (174–216 amu) of effusate from  $\text{LaF}_3 + \text{PrF}_3 + \text{HoF}_3 + \text{LuF}_3$  at 1120 °C. Intensity of largest (213 amu) peak is  $8 \times 10^{-10}$  A.

these experiments. In addition to the dominant  $\text{LnF}_2^+$  fragment peaks (177 amu,  $\text{LaF}_2^+$ ; 179,  $\text{PrF}_2^+$ ; 203,  $\text{HoF}_2^+$ ; 213,  $\text{LuF}_2^+$ ), the minor  $\text{HoF}^+$  and  $\text{LuF}^+$  fragment peaks appear at 184 and 194 amu, respectively. The peak at 198 amu may be due to  $\text{PrF}_3^+$ . Only the broad (weak) peak around 207 amu in this spectrum was non-shutterable; it is considered to be due to  $\text{Pb}^+$ , arising from re-evaporation of lead metal previously deposited inside the vacuum chamber.

Examination of the fluoride residues after the high temperature measurements indicated that fusion of the mixture had occurred during each experiment. Furthermore, the continuity of the observed mass signals versus temperature suggested that fusion had occurred prior to measurable vaporization of the fluorides. This is based on the contention that the resultant drop in the concentration of each component upon solution formation at the fusion point would be reflected in a discontinuous drop in vapor pressure/ion intensity. Such behavior suggests significant melting point depressions for certain of the fluorides in these mixtures (i.e., up to  $400^\circ\text{C}$  below the reported  $\text{LaF}_3$  melting point of  $1500^\circ\text{C}$  [3] in the case of the  $\text{LaF}_3 + \text{PrF}_3 + \text{HoF}_3 + \text{LuF}_3$  mixture). Phase diagrams of several  $\text{LnF}_3\text{-Ln}'\text{F}_3$  systems have been experimentally determined [4] and large melting point depressions are reported in some cases. For example, a eutectic at 31 %  $\text{LaF}_3$ /69%  $\text{LuF}_3$  and  $1038^\circ\text{C}$  is over  $450^\circ\text{C}$  below the melting point of pure  $\text{LaF}_3$ . A small amount of metallic deposit on the resolidified fluoride residues was observed. The quantity was too small to retrieve for analysis and it was assumed to be reprecipitated tantalum metal.

### *Interpretation of measurements*

As discussed above, of particular interest is the derivation of relative enthalpies of vaporization ( $\Delta\Delta H_{\text{vap}}(\text{LnF}_3\text{-Ln}'\text{F}_3)$ ) from the mass spectroscopic measurements made in this study. The values of Second Law  $\Delta\Delta H$  may be obtained from van 't Hoff plots of the temperature dependence of the ion intensities, while corresponding Third Law values may be derived from each measured relative intensity (vapor pressure) provided a reasonable estimate for  $\Delta\Delta S_{\text{vap}}$  can be made.

Since no significant variation in either the slopes of  $\ln(I(\text{LnF}_x^+) \cdot T)$  vs.  $1/T$ , or the ratios of the  $I(\text{LnF}_2^+)$  for the different Ln of a given mixture was detected as a function of temperature, it was concluded that the data obtained here are for liquid fluoride solutions (see above). The trivalent lanthanide halides (excluding  $\text{SmX}_3$ ,  $\text{EuX}_3$ , and  $\text{YbX}_3$  which may reduce to lower halides) are all chemically very similar and mixtures of them should behave as nearly ideal solutions (i.e.,  $\Delta H_{\text{mix}} \sim \Delta S_{\text{mix,excess}} \sim 0$ ). In accord with this is the result of a calorimetric study of the system  $\text{LaCl}_3\text{-GdCl}_3$  [5], which indicated only a very small enthalpy of mixing ( $< 0.2 \text{ kcal mol}^{-1}$  at the composition  $(\text{LaCl}_3)_{0.5}(\text{GdCl}_3)_{0.5}$ ). When ideal solution formation is

assumed, a correction need not be made to Second Law enthalpies and only the dilution factor need be applied to measured pressures in order to obtain the vapor pressures for the pure materials.

### *Second Law method*

Using the relationship between the measured mass spectral intensities for some ion fragment of vapor species,  $i$ ,  $i^+$ , and the pressure of that species in the Knudsen cell,  $P_i = k_{i^+} \cdot I_{i^+} \cdot T$  [6], Second Law enthalpies of vaporization may be derived from plots of the temperature dependence of  $I_{i^+}$ , by using the van 't Hoff relationship

$$d \ln P / d(1/T) = d \ln(I \cdot T) / d(1/T) = -\Delta H / R \quad (1)$$

Similarly, relative vaporization enthalpies may be obtained by difference through the relationship

$$d \ln(I_b / I_a) / d(1/T) = \Delta H_a / R - \Delta H_b / R = \Delta \Delta H_{a-b} / R \quad (2)$$

A typical set of data from which Second Law enthalpies can be derived are plotted in Fig. 3. The two upper van 't Hoff plots are of mass spectral intensities obtained simultaneously for  $\text{HoF}_2^+$  and  $\text{TmF}_2^+$  and the slopes indicate vaporization enthalpies of close to  $100 \text{ kcal mol}^{-1}$  for both  $\text{HoF}_3$ , and  $\text{TmF}_3$  in this  $\text{HoF}_3 + \text{TmF}_3$  mixture. Essentially the same deviations from the linear fit are evident for many of the corresponding points (same  $T$ ) in the two data sets, confirming that some significant errors will be cancelled when the ratio, or difference, of two such data sets is considered (of course the effects of systematic errors are not so evident). The difference van 't Hoff plot for these two data sets is shown at the bottom of Fig. 3; although the scatter in this plot appears large, the  $y$ -axis scale has been greatly expanded relative to the upper plots and the slope corresponds to a  $\Delta \Delta H_{\text{vap}}(\text{HoF}_3 - \text{TmF}_3)$  value of only  $0.5 \text{ kcal mol}^{-1}$ . Whereas an uncertainty of perhaps  $10 \text{ kcal mol}^{-1}$  might be associated with the individual  $\Delta H_{\text{vap}}^{\text{II}}$  values, the  $\Delta \Delta H_{\text{vap}}^{\text{II}}$  obtained here may be considered to be accurate to within about  $2 \text{ kcal mol}^{-1}$ . This latter uncertainty is still larger than desirable for resolving the details of  $\text{LnF}_3$  vaporization thermodynamics, and the Second Law results have been primarily used to confirm qualitatively the results of the Third Law method described below.

### *Third Law method*

The so-called Third Law method typically requires an equilibrium constant ( $P^0(\text{LnF}_3)$  in this case) from which  $\Delta G (= -RT \ln K)$  may be obtained, and absolute entropies for the reactants and products from which  $\Delta S$  for the net reaction may be obtained. In the present study, relative  $P^0(\text{LnF}_3)$  are derived from measured  $I(\text{LnF}_2^+)$  to yield  $\Delta \Delta G_{\text{vap}}$ ; and  $\Delta \Delta S_{\text{vap}}$  are estimated (without reference to absolute entropies) so that  $\Delta \Delta H_{\text{vap}}^{\text{III}}$  may be obtained.

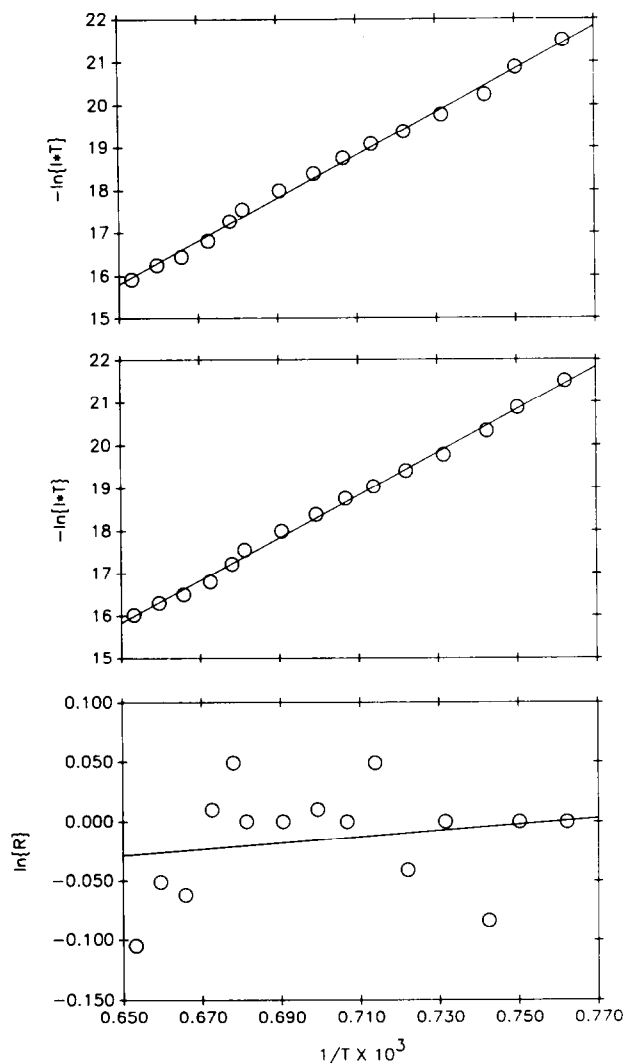


Fig. 3. Results of vaporization study of  $\text{HoF}_3 + \text{TmF}_3$ . Top:  $I = I(\text{HoF}_2^+)(A)$ ;  $\Delta H_{\text{vap}}^{\text{II}}(\text{HoF}_3)(1150^\circ\text{C}) = 99.7 \text{ kcal mol}^{-1}$ . Middle:  $I = I(\text{TmF}_2^+)(A)$ ;  $\Delta H_{\text{vap}}^{\text{II}}(\text{TmF}_3)(1150^\circ\text{C}) = 99.3 \text{ kcal mol}^{-1}$ . Bottom:  $R = I(\text{TmF}_2^+)/I(\text{HoF}_2^+)$ ;  $\Delta \Delta H_{\text{vap}}^{\text{II}}(\text{HoF}_3 - \text{TmF}_3) = 0.5 \text{ kcal mol}^{-1}$ .

In order to determine absolute vapor pressures from mass spectrometric data, the calibration constant,  $k$  in the relation  $P = k \cdot I \cdot T$ , must be known for the measured ion fragment of the vapor species of interest. Mass spectrometric intensities determined simultaneously can be converted to relative pressures by estimating the difference between the calibration constants for the two ion fragments,  $\text{LnF}_2^+$  and  $\text{Ln}'\text{F}_2^+$ . Factors affecting the calibration constant include detector efficiency, experimental geometry, ionization efficiency, and fragmentation pattern ( $\text{LnF}_3 \rightarrow \text{LnF}_x^{y+} + (3 -$

$x)F^{z+}$ ). The similarity of the trivalent lanthanide fluorides studied here somewhat simplified the situation. The detector (quadrupole) efficiency, including multiplier gain, should be essentially the same for all of these  $\text{LnF}_2^+$  ions of similar mass (177–213 amu). Further, the inherent advantage of the technique of studying mixtures is that the experimental geometry is identical for all of the components. The ionization cross sections ( $\sigma$ ) of the lanthanide elements studied here ( $\sigma(\text{Ln}^0)$ ) are given by Mann [7] and differ by as much as 40% from one another. However,  $\sigma(\text{LnF}_3)$  will consist of some significant contribution from  $\sigma(\text{F}^-)$  as well as of some (presumably less important) contribution from  $\sigma(\text{Ln}^{3+})$ , and the variation in  $\sigma(\text{LnF}_3)$  for the lanthanides studied here should be significantly less than 40%.

That the particular fragmentation pattern for the  $\text{LnF}_3$  depends upon the lanthanide element being studied is illustrated by the mass spectrum shown in Fig. 2 where  $I(\text{HoF}^+; 184 \text{ amu})/I(\text{HoF}_2^+; 203 \text{ amu}) < I(\text{LuF}^+; 194 \text{ amu})/I(\text{LuF}_2^+; 213 \text{ amu})$ . For each of the fluorides studied, however, the dominant  $\text{LnF}_2^+$  fragment ion (of the  $\text{LnF}_3$  neutral) peak is approximately ten times more intense than the next most significant fragment ion and thus provides a reliable monitor of the total  $I(\sum(\text{LnF}_x^{y+}))$  relative to  $I(\sum(\text{Ln}'\text{F}_x^{y+}))$ . The natural isotopic abundances were used to adjust the measured (most abundant)  $\text{LnF}_2^+$  peak when more than one isotope of a particular Ln was significant.

The above considerations allow the approximation that all of the calibration constants ( $k$ ) are essentially the same in the equation,  $P(\text{LnF}_3) = k(\text{LnF}_2^+) \cdot I(\text{LnF}_2^+) \cdot T$ . The ratios of the pure lanthanide trifluoride vapor pressures are then obtained from the measurements over the mixture of composition  $(\text{LnF}_3)_x(\text{Ln}'\text{F}_3)_y$  by applying the ideal dilution correction

$$P(\text{LnF}_3)/P(\text{Ln}'\text{F}_3) = (I(\text{LnF}_2^+)/I(\text{Ln}'\text{F}_2^+))(y/x) \quad (3)$$

It is assumed that  $\Delta\Delta S_{\text{vap}}(\text{LnF}_3-\text{Ln}'\text{F}_3) \cong 0 \pm 1 \text{ cal mol}^{-1} \text{ K}^{-1}$  for the trivalent lanthanide halides in which the trivalent oxidation state of the lanthanide species is considered fixed (i.e., excluding  $\text{SmX}_3$ ,  $\text{EuX}_3$ , and  $\text{YbX}_3$ ). Magnetic and electronic entropy effects, which are specific to each  $\text{Ln}^{3+}$  ion, cancel out between the condensed and gaseous states for a constant valence state. Because the bonding in all of the  $\text{LnF}_3$  is expected to be very similar, variations in their  $\Delta S_{\text{vap}}$  should be small. This is particularly true for liquid fluorides (as studied here) since potential differences between crystal structures need not be considered. Reported variations in  $\text{LnF}_3$  vaporization entropies of up to  $15 \text{ cal mol}^{-1} \text{ K}^{-1}$  (i.e.,  $\text{NdF}_3 = 36.7$  compared with  $\text{ErF}_3 = 51.9$ ) [2] are therefore rather surprising in light of the above considerations. Comparison with other lanthanide trihalide vaporization studies suggests that systematic errors may be particularly relevant in explaining such variations. In the case of the lanthanide tribromides, for example, the  $\Delta S_{\text{vap}}[\text{LnBr}_3; \text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}]$  from ref. 8 are all  $42.7 \pm 0.6 \text{ cal mol}^{-1} \text{ K}^{-1}$  while those for  $\text{Ln} = \text{Gd}, \text{Tb}, \text{Dy}, \text{Er}, \text{Tm}, \text{Lu}$  from ref. 9 are



some 18 cal mol<sup>-1</sup> K<sup>-1</sup> lower but are all within 2 cal mol<sup>-1</sup> K<sup>-1</sup> of each other.

Having obtained the  $R_{a-b} = P(\text{Ln}^a\text{F}_3)/P(\text{Ln}^b\text{F}_3)$  as described above (eqn. (3)) and using the estimate that  $\Delta\Delta S_{\text{vap}}(\text{Ln}^a\text{F}_3-\text{Ln}^b\text{F}_3) \cong 0 \pm 1$  cal mol<sup>-1</sup> K<sup>-1</sup>, relative Third Law enthalpies of vaporization may be obtained through the following (where  $\Delta\Delta H_{a-b} = \Delta H_{\text{vap}}(\text{Ln}^a\text{F}_3) - \Delta H_{\text{vap}}(\text{Ln}^b\text{F}_3)$ )

$$\Delta\Delta G_{a-b} = -RT \ln(R_{a-b}) = \Delta\Delta H_{a-b} - T\Delta\Delta S_{a-b} = \Delta\Delta H_{a-b} \quad (4)$$

### *Relative vapor pressures and enthalpies of vaporization*

The results for the four (labeled I–IV) lanthanide trifluoride mixtures studied are compiled in Table 1. Relative vapor pressures/enthalpies of vaporization are tabulated for selected pairs within each mixture: values for other pairs within the multicomponent mixtures can be derived from the values given. In the final column (for purposes of comparison with the results obtained here) the corresponding difference enthalpies from ref. 1 are

TABLE 1

Relative vapor pressures and enthalpies of vaporization of lanthanide trifluorides

LnF <sub>3</sub> compared	Temperature range (°C)	P <sub>a</sub> /P <sub>b</sub>	ΔΔ <sup>III</sup> <sub>vap,a-b</sub> (kcal mol <sup>-1</sup> )	ΔΔ <sup>II</sup> <sub>vap,a-b</sub> (kcal mol <sup>-1</sup> )	ΔΔ <sup>I</sup> <sub>vap,a-b</sub> [1] (kcal mol <sup>-1</sup> )
I 1.35HoF <sub>3</sub> + 1.00TmF <sub>3</sub>					
a = HoF <sub>3</sub> b = TmF <sub>3</sub>	1040–1260	0.77	0.7	0.5	4.6
II 1.00TbF <sub>3</sub> + 1.05HoF <sub>3</sub> + 1.10LuF <sub>3</sub>					
a = TbF <sub>3</sub> b = LuF <sub>3</sub>	1090–1270	0.67	1.2	2	2.1
a = HoF <sub>3</sub> b = LuF <sub>3</sub>	1090–1270	0.82	0.6	1.8	4.8
III 1.35LaF <sub>3</sub> + 1.00GdF <sub>3</sub> + 1.23LuF <sub>3</sub>					
a = LaF <sub>3</sub> b = LuF <sub>3</sub>	1200–1260	0.06	8	–	0.2
a = GdF <sub>3</sub> b = LuF <sub>3</sub>	1160–1260	0.50	2.1	–	4.1
IV 1.18LaF <sub>3</sub> + 1.00PrF <sub>3</sub> + 1.24HoF <sub>3</sub> + 1.13LuF <sub>3</sub>					
a = LaF <sub>3</sub> b = PrF <sub>3</sub>	1000–1250	0.91	0.2	–0.1	1.0
a = LaF <sub>3</sub> b = LuF <sub>3</sub>	1000–1250	0.05	8	15	0.2
a = HoF <sub>3</sub> b = LuF <sub>3</sub>	900–1250	0.74	0.8	3	4.8

shown. For those pairs which were studied in more than one mixture (HoF<sub>3</sub> and LuF<sub>3</sub>, II and IV; LaF<sub>3</sub> and LuF<sub>3</sub>, III and IV) the consistency of the results is good. As discussed above, the Second Law results are considered ancillary and the Third Law values are emphasized as the more reliable (Second Law values were not obtained where the temperature range was considered inadequate).

From the values for  $\Delta\Delta H_{\text{vap}}(\text{LnF}_3)$  obtained here, the following conclusions result regarding the relative values suggested in ref. 1 and shown in Fig. 1. The HoF<sub>3</sub> and TmF<sub>3</sub> (I), HoF<sub>3</sub> and TbF<sub>3</sub> (II), and HoF<sub>3</sub> and LuF<sub>3</sub> (II and IV) results suggest that the maximum at HoF<sub>3</sub> does not exist. Instead, there appears to be a gradual monotonic decrease in  $\Delta H_{\text{vap}}$  with increasing atomic number in this region of the lanthanide series. Similarly, the GdF<sub>3</sub> and LuF<sub>3</sub> (III) study may be taken to indicate a small cusp at GdF<sub>3</sub> but not a peak of the magnitude suggested in Fig. 1.

Based upon the LnI<sub>3</sub>, LnBr<sub>3</sub> and LnCl<sub>3</sub> vaporization thermodynamics systematics (see Fig. 1), it would be expected that a drop in  $\Delta H_{\text{vap}}$  of at least  $\sim 6 \text{ kcal mol}^{-1}$  would occur across the lanthanide trifluoride series. It is thus surprising that the values from ref. 1 (see Fig. 1) suggest essentially no net decrease in going from LaF<sub>3</sub> to LuF<sub>3</sub>. In contrast, the results reported here for LaF<sub>3</sub> and LuF<sub>3</sub> (III and IV), and PrF<sub>3</sub> and LuF<sub>3</sub> (IV) indicate a decrease in  $\Delta H_{\text{vap}}$  of  $\sim 8 \text{ kcal mol}^{-1}$  between LaF<sub>3</sub>/PrF<sub>3</sub> and LuF<sub>3</sub>.

It should be noted that the values for  $\Delta H_{\text{sub}}(\text{LnF}_3)$  given in ref. 1 are for the solid fluorides at 298 K whereas those obtained here are for liquids at elevated temperature. Condensed fluoride enthalpies determined by Spedding and coworkers [10,11] suggest that liquid trifluoride relative vaporization thermodynamics, as obtained here, may reasonably be compared with corresponding values for the solids. The  $\Sigma\Delta H_{\text{trans}} + \Delta H_{\text{fusion}}$  from refs. 10 and 11 are within  $3 \text{ kcal mol}^{-1}$  of one another for all of the lanthanide trifluorides studied here.

## CONCLUSIONS

This investigation of the vaporization thermodynamics of mixed lanthanide trifluoride systems has provided relative enthalpies of vaporization which describe the trend across the series more reliably than those derived from the comparison of data from independent experiments involving individual fluoride samples. Values from this study of relative enthalpies of vaporization are plotted in Fig. 4, where  $\Delta\Delta H_{\text{vap}}(\text{LuF}_3)$  has been assigned a relative value of zero and the other  $\Delta\Delta H_{\text{vap}}$  are thus relative to LuF<sub>3</sub> ( $\Delta\Delta H_{\text{vap}}(\text{LnF}_3) \equiv \Delta H_{\text{vap}}(\text{LnF}_3) - \Delta H_{\text{vap}}(\text{LuF}_3)$ ). The results obtained here for the selected fluoride pairs are in contrast to the previous suggestion [1] (Fig. 1) of the possibility of rather irregular variations in  $\Delta H_{\text{vap}}(\text{LnF}_3)$  across the lanthanide series. Rather, the trifluoride vaporization thermody-

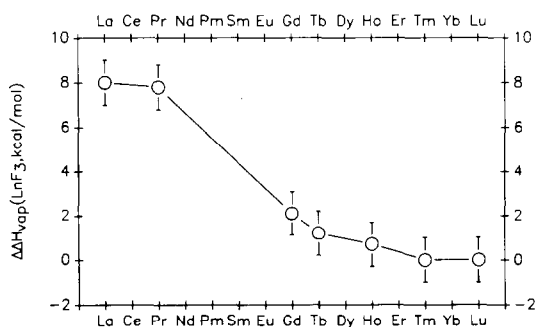


Fig. 4. Relative enthalpies of vaporization of selected  $\text{LnF}_3$  obtained in this study.  $\text{LuF}_3$  has been assigned a value of zero so that  $\Delta\Delta H_{\text{vap}}(\text{LnF}_3) \equiv \Delta H_{\text{vap}}(\text{LnF}_3) - \Delta H_{\text{vap}}(\text{LuF}_3)$ .

namic systematics derived from this work suggest a smoother decrease in  $\Delta H_{\text{vap}}$  across the lanthanide series, in accord with the corresponding trend exhibited by other lanthanide trihalides [1].

#### ACKNOWLEDGMENT

This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

#### REFERENCES

- 1 C.E. Myers and D.T. Graves, *J. Chem. Eng. Data*, 22 (1977) 440.
- 2 K.F. Zmbov and J.L. Margrave, in R.F. Gould (Ed.), *Mass Spectrometry in Inorganic Chemistry*, American Chemical Society, Washington, D.C., 1968, p. 267.
- 3 D. Brown, *Halides of the Lanthanides and Actinides*, Wiley-Interscience, New York, 1968, Chap. 2.
- 4 B.P. Sobolev, P.P. Fedorov, A.K. Galkin, V.S. Sidorov, and D.D. Ikrami, in V.S. Sidorov (Ed.), *Growth of Crystals*, Vol. 13, Consultants Bureau, New York, 1986, p. 229.
- 5 R. Balchnik and E. Enninga, *Thermochim. Acta*, 78 (1984) 427.
- 6 O. Kubaschewski and C.B. Alcock, *Metallurgical Thermochemistry*, 5th edn., Pergamon, New York, 1979, p. 143.
- 7 J.B. Mann, *J. Chem. Phys.*, 46 (1967) 1646.
- 8 E. Shimazaki and K. Niwa, *Z. Anorg. Allg. Chem.*, 314 (1962) 21.
- 9 A. Makhmadmurodov, G.P. Dudchik, and O.G. Polyachenok, *Russ. J. Phys. Chem.*, 49 (1975) 1599.
- 10 F.H. Spedding and D.C. Henderson, *J. Chem. Phys.*, 54 (1970) 2476.
- 11 F.H. Spedding, B.J. Beaudry, D.C. Henderson and J. Moorman, *J. Chem. Phys.*, 60 (1974) 1578.