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A comparative investigation on the thermodynamics of vaporization of LaF_3 and LuF_3

T. Petzel, V. Marx, J. Potthast and Th. Ahnen

Universität der Bundeswehr, Institut für Werkstofftechnik, Holstenhofweg 85, W-2000 Hamburg 70 (Germany)

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Abstract

The vapour pressure curves of $LaF_3(s)$ and $LuF_3(l)$ were measured by the Knudsen effusion weight loss method using carefully calibrated molybdenum and graphite Knudsen cells. The following vapour pressure equations were obtained (with standard deviations). $LaF_3(s)$: $\ln p = (-50363 \pm 778)T^{-1} + (22.136 \pm 0.507)$. $LuF_3(l)$: $\ln p = (-42181 \pm 1049)T^{-1} + (15.993 \pm 0.627)$.

Second and third law extrapolations yielded the following standard enthalpies and entropies of vaporization. $LaF_3(s)$: $\Delta_v H^\circ_{298}(II) = 456.3 \pm 8.3$ kJ mol^{-1}; $\Delta_v S^\circ_{298}(II) = 229.7 \pm 10.1$ J mol^{-1} K^{-1}; $\Delta_v H^\circ_{298}(III) = 433.0 \pm 7.9$ kJ mol^{-1}; $\Delta_v S^\circ_{298}(III) = 214.6$ J mol^{-1} K^{-1}. $LuF_3(s)$: $\Delta_v H^\circ_{298}(II) = 441.8 \pm 10.8$ kJ mol^{-1}; $\Delta_v S^\circ_{298}(II) = 213.6 \pm 11.1$ J mol^{-1} K^{-1}; $\Delta_v H^\circ_{298}(III) = 453.2 \pm 9.2$ kJ mol^{-1}; $\Delta_v S^\circ_{298}(III) = 220.4$ J mol^{-1} K^{-1}.

These results are critically compared with the respective data from the literature. An additional third law treatment led to enthalpies of vaporization at 1500 K for both trifluorides in the liquid state. ($\Delta_v H^\circ_{1500}(III)$ $[LaF_3(l)] = 395.6$ kJ mol^{-1}; $\Delta_v H^\circ_{1500}(III)$ $[LuF_3(l)] = 370.5$ kJ mol^{-1}) and hence to $\Delta\Delta_v H^\circ_{1500}[LaF_3(l) - LuF_3(l)] = 25.1$ kJ mol^{-1}. This difference at 1500 K is found to be in reasonable agreement with a corresponding result from the literature, 33 kJ mol^{-1}, derived from relative vapour pressure measurements on liquid lanthanoid trifluoride mixtures.

INTRODUCTION

The lanthanoid trifluorides are a group of compounds whose standard enthalpies of vaporization, derived from high temperature vapour pressure measurements, all lie within a range of 431–449 kJ mol^{-1} [1,2]. Because of this noteworthy similarity, and considering the uncertainties of the data of 2–15 kJ mol^{-1}, it is not surprising that the reported enthalpies vary rather irregularly across the lanthanoid series and cannot be correlated in a meaningful way. Recently Gibson and Haire [3] have studied the vaporization thermodynamics of selected liquid mixed LnF_3 systems by high temperature mass spectrometry and have derived relative enthalpies of vaporization which, contrary to the above mentioned situation for the absolute standard values, follow a regular trend across the series, which resembles the corresponding trends for the lanthanoid tribromides and triiodides. This trend can be described as a smooth decrease in $\Delta_v H$ from LaF_3 to LuF_3, the difference between the values for the end members of the trifluoride series being 33 kJ mol^{-1} at about 1500 K. However, if the third law $\Delta_v H^\circ_{298}$ for solid LaF_3 reported by Mar and Searcy [4] and for solid LuF_3 by Zmbov and Margrave [5] are considered, the standard enthalpies of sublimation of both trifluorides are practically equal. This discrepancy could be due, at least in part, to the reported low accuracy of the value for LuF_3, 437 ± 17 kJ mol^{-1} [5]. According to our experience it should be possible by careful absolute Knudsen effusion weight-loss measurements to verify a difference of about 33 kJ mol^{-1} between the enthalpies of vaporization of two physically and chemically similar compounds like LaF_3 and LuF_3, for which the standard entropies, the enthalpy and free energy functions and the enthalpies of transition and fusion are known with reasonable accuracy (refs. 6–9).

In this paper the results of absolute vapour pressure measurements on LaF_3 and LuF_3 are reported, and the systematics of the vaporization thermodynamics of these lanthanoid trifluorides are discussed with special reference to the work of Gibson and Haire [3].

EXPERIMENTAL

Preparation and characterization of substances

The LaF_3 and LuF_3 were prepared by dissolution of the sesquioxides (stated purity 99.99%, Auer-Remy KG) in hydrochloric acid, precipitation of the hydrated trifluorides with hydrofluoric acid, drying at 390 K in air and subsequent dehydration under a gas stream of dry HF/N_2 at 1000 K. For a further purification, LuF_3 was distilled inside a tubular molybdenum crucible in a high vacuum at 1570 K in order to remove any traces of oxide impurities, which might have formed during the annealing procedure in the HF atmosphere. The trifluorides can be purified by distillation, because oxide fluoride impurities like, for example, LuOF decompose according to reaction (1)

$$3\,LuOF(s) \rightarrow LuF_3(g) + Lu_2O_3(s) \qquad (1)$$

The trifluorides were characterized by their X-ray powder diffraction patterns [Guinier method, Cu $K\alpha_1$ radiation, silicon (reference material NBS 640 A) as internal calibration standard], and the lattice parameters were calculated using a least squares computer program. The compounds proved to be very well crystallized, and the powder patterns did not display any diffraction lines of other phases. The lattice parameters were in very good agreement with the precision data reported by Greis and Petzel [10]; see Table 1. Both compounds were further characterized by determination

TABLE 1

Data for the structural and thermal characterization of LaF_3 and LuF_3

Compound	Lattice parameters (pm)			Ref.	1st order transformations (K)		Ref.
	a	b	c		T_{trans}	T_{fus}	
LaF_3	718.7	–	735.1	This work	–	1768	This work
	718.6	–	735.0	10	–	1766	6
					–	1773	11, 12
LuF_3	614.4	676.0	447.1	This work	1231	1457	This work
	615.0	676.2	446.8	10	1230	1457	6
					1236	1455	11
					1216	1453	12

of the phase transition and melting temperatures by differential thermal analysis performed in a Netzsch STA 429 apparatus. For the DTA measurements the samples were enclosed in gas tight platinum ampoules. The thermal results listed in Table 1 are also in good agreement with data from the literature [6,11,12].

Knudsen effusion measurements, apparatus and procedure

The vapour pressure measurements were carried out by the Knudsen effusion weight-loss technique using cylindrical molybdenum Knudsen cells with effective orifice areas of 4.548×10^{-3} cm^2 (cell A), 2.700×10^{-3} cm^2 (cell B) and two graphite cells with respective values of 2.398×10^{-4} and 6.302×10^{-4} cm^2 (cells C1 and C2). The cells were heated by radiation from an inductively heated cylindrical tantalum susceptor in a high vacuum ($p \leq 10^{-5}$ mbar) inside a water cooled silica tube. The temperature was measured by sighting an optical pyrometer (Leeds & Northrup, type 8632-C, or Keller, type PB 06 AF3) onto a cylindrical black-body cavity in the bottom of the cell via an optical window and a prism. The temperature readings were corrected for the insertion of the window and the prism. The effused mass was determined by weighing the cell before and after each experiment, and the time was measured with a high precision electronic clock. In order to establish a satisfactory accuracy of the temperature measurements, which is of crucial importance for the accurate evaluation of the enthalpy and entropy data, the cells were calibrated by measuring the vapour pressures of liquid tin (stated purity 99.99995%, Ventron). By comparing the experimental results with well established vapour pressure data for tin from the literature [13], appropriate corrections could be applied to the temperature readings. The overall accuracy of the temperature measurements was considered to be ±5 K. Total vaporization experiments with samples of LaF_3 and LuF_3 resulted in weight losses of the cell materials of less than 0.1 mg in each case, and it was hence concluded that molybdenum and graphite are chemically inert towards both trifluorides. Rates of effusion with a total of 18 data points for LaF_3 (cells A and B) and a total of 25 points for LuF_3 (16 points with cell B and nine points with cells C1 and C2) were measured over the temperature ranges 1419–1661 K (LaF_3) and 1471–1945 K (LuF_3).

Thermodynamic evaluation of effusion results

The amount of gaseous species i, m_i (g) of molar mass M_i (g mol^{-1}) effused in time t (s) at temperature T (K) from a Knudsen cell with an effective orifice area a (cm^2) is related to the partial equilibrium pressure of species i, p_i (bar), inside the cell by the Knudsen equation

$$p_i = \frac{m_i}{at}\left(\frac{2\pi RT}{M_i}\right)^{1/2} = \frac{m_i}{43.7519at}\left(\frac{T}{M_i}\right)^{1/2} \qquad (2)$$

For solid- and liquid–gas equilibria of the lanthanoid trifluorides in the pressure range which is typical of Knudsen effusion experiments, the dominant mode of vaporization is represented by

$$LnF_3(c) \rightarrow LnF_3(g) \qquad (3)$$

The equilibrium content of the dimer Ln_2F_6 in the gas phase is $\leq 1\%$ at 1575 K in the case of LaF_3 [14,15]. Assuming a similar situation for LuF_3, it can thus be safely concluded that no significant error is introduced if the vapour pressure calculations are exclusively based on reaction (3). The vapour pressure curves of LaF_3 and LuF_3 are outlined in Fig. 1 and the experimental data are collected in Tables 2 and 3. Linear least squares treatments of the data yielded the vapour pressure equations (4) and (5) (with standard deviations)

$$LaF_3 \quad \ln p = (-50\,363 \pm 778)T^{-1} + (22.136 \pm 0.507) \qquad (4)$$

$$LuF_3 \quad \ln p = (-42\,181 \pm 1049)T^{-1} + (15.993 \pm 0.627) \qquad (5)$$

From these equations the following enthalpies and entropies of vaporization were derived for the median temperatures of the measurements, 1540 K (LaF_3) and 1708 K (LuF_3).

$$LaF_3 \quad \Delta_v H^\circ_{1540} = 418.7 \pm 6.5 \text{ kJ mol}^{-1}$$

$$\Delta_v S^\circ_{1540} = 184.1 \pm 4.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$LuF_3 \quad \Delta_v H^\circ_{1708} = 350.7 \pm 8.7 \text{ kJ mol}^{-1}$$

$$\Delta_v S^\circ_{1708} = 133.0 \pm 5.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

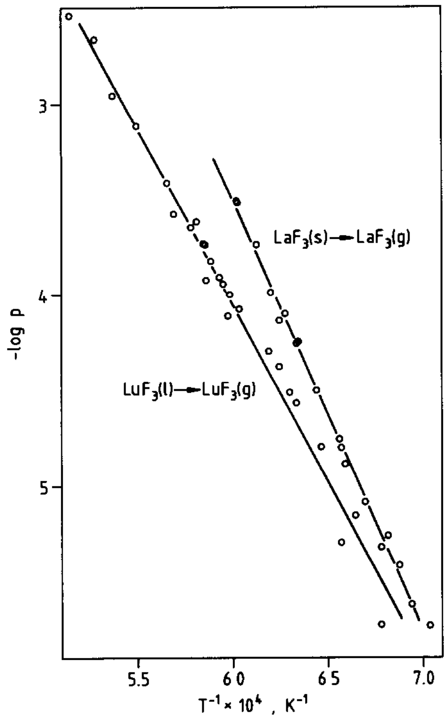

Fig. 1. Vapour pressure curves of LaF_3(s) and LuF_3(l).

TABLE 2

Vaporization data of LaF_3(s)

T (K)	p (bar)	$\Delta_v H^\circ_{298}$(III) (kJ mol^{-1})
1419	1.88E−6	434.0
1438	2.43E−6	436.1
1450	3.87E−6	433.7
1465	5.40E−6	433.8
1471	4.83E−6	436.7
1491	8.28E−6	435.2
1514	1.30E−5	435.4
1519	1.57E−5	434.4
1521	1.72E−5	433.7
1549	3.14E−5	433.1
1573	5.64E−5	431.3
1575	5.55E−5	431.9
1590	7.79E−5	430.9
1598	7.22E−5	433.9
1611	9.89E−5	432.6
1633	1.79E−4	429.8
1660	3.01E−4	428.6
1661	3.09E−4	428.4

TABLE 3

Vaporization data of $LuF_3(l)$

T [a] (K)	p (bar)	$\Delta_v H^\circ_{298}$(III) (kJ mol^{-1})
1471	1.88E−6	457.5
1503	7.01E−6	449.2
1519	5.12E−6	457.2
1545	1.61E−5	448.9
1576	2.74E−5	449.0
1586	3.13E−5	449.6
1600	4.23E−5	448.8
1613	5.09E−5	449.2
1665	8.47E−5	454.0
1670	1.01E−4	452.5
1672	7.86E−5	456.6
1680	1.14E−4	453.1
1687	1.24E−4	453.4
1703	1.53E−4	453.9
1705	1.21E−4	457.6
1710	1.83E−4	452.8
1711	1.85E−4	452.8
1720	2.44E−4	450.9
1732	2.28E−4	454.4
1757	2.97E−4	455.8
1769	3.92E−4	454.2
1819	7.83E−4	454.0
1861	1.13E−3	456.4
1897	2.20E−3	452.8
1945	2.96E−3	456.7

[a] Points at $T = 1670$, 1703 and 1732–1945 K measured with undistilled samples.

Extrapolations to 298 K by the second and third law methods using the interpolation formulae from ref. 2 for the enthalpy and the free energy functions of $LnF_3(g)$ based on measurements as in ref. 7, the respective data for $LnF_3(c)$ from ref. 6 and the standard entropies from [8,9] resulted in the following standard enthalpies of vaporization

$$LaF_3 \quad \Delta_v H^\circ_{298}(\mathrm{II}) = 456.3 \pm 8.3 \text{ kJ mol}^{-1}$$

$$\Delta_v H^\circ_{298}(\mathrm{III}) = 433.0 \pm 7.9 \text{ kJ mol}^{-1}$$

$$LuF_3 \quad \Delta_v H^\circ_{298}(\mathrm{II}) = 441.8 \pm 10.8 \text{ kJ mol}^{-1}$$

$$\Delta_v H^\circ_{298}(\mathrm{III}) = 453.2 \pm 9.2 \text{ kJ mol}^{-1}$$

The third law enthalpies for the individual data points are included in Tables 2 and 3. The second law accuracy limits follow from the standard deviations of the measurements and the errors of the enthalpy and entropy functions given in the literature. The third law accuracy limits were calculated from the standard deviations of the measurements and the errors of the free energy functions and the standard entropies. The second and third law enthalpies are in very good agreement, and the third law results show a slight (LaF_3) and an almost negligible (LuF_3) trend with temperature.

DISCUSSION

The calculated third law difference $\Delta\Delta_v H^\circ_{298}[LaF_3 - LuF_3] = -20.2$ kJ mol^{-1} deviates significantly from the corresponding value of Gibson and Haire [3] for the liquid compounds at 1500 K, +33 kJ mol^{-1}. These data are not unambiguously comparable because of the temperature difference and the different states of the condensed phases at 298 K. Therefore the data should be referred to the common temperature of 1500 K, as well as to an identical condensed state, here the liquid state, because LaF_3 crystallizes in the tysonite structure, whereas LuF_3 crystallizes in the β- and α-YF_3-type structures. The thermodynamic quantities to be used for a data re-evaluation are the third law standard enthalpies of sublimation from this work, the standard entropies [8,9], the enthalpy and free energy functions [2,6] and the enthalpies of transformation and fusion [6]. Important criteria for a judgement of the accuracy of thermodynamic data derived from equilibrium measurements are, firstly, the agreement of the second and third law enthalpies and entropies of reaction and, secondly, the absence of a significant dependence of the third law enthalpy on temperature, provided the free energy functions are accurately known. It has now to be shown that the accuracy of our third law results justifies their use in a comparative discussion with the result of Gibson and Haire [3]. All currently available experimentally based data concerning the vaporization thermodynamics of LaF_3 and LuF_3 are summarized in Table 4. Since experimental values from refs. 6–9 for enthalpy and entropy functions were

TABLE 4

Second and third law standard enthalpies (kJ mol^{-1}) and entropies (J mol^{-1} K^{-1}) of sublimation of LaF_3 and LuF_3

Compound	$\Delta_v H^\circ_{298}$(II)	$\Delta_v H^\circ_{298}$(III)	$\Delta_v S^\circ_{298}$(II)	$\Delta_v S^\circ_{298}$(III)	Ref.
LaF_3	456.3 ± 8.3	433.0 ± 7.9	229.7 ± 10.1	–	this work
	453.0 ± 3.8	431.9 ± 7.6	229.1 ± 7.2	–	4
	378.4 ± 8.8	430.1 ± 7.3	178.7 ± 10.8	–	17
	412.0 ± 5.4	440.3 ± 6.6	193.2 ± 8.6	–	16
	–	–	–	214.6 ± 0.3	2,7,8
LuF_3	441.8 ± 10.8	453.2 ± 9.2	213.6 ± 11.1	–	this work
	451.4 ± 3.9	435.2 ± 7.1	232.6 ± 14.6	–	5
	–	–	–	220.4 ± 0.3	2,7,9

not available to the authors of refs. 4, 5, 16 and 17, it was necessary to revise the second and third law calculations in order to obtain data which are comparable with the results of this work. For LaF_3 our second and third law data agree very well and are, furthermore, in excellent agreement with the results of Mar and Searcy [4], who measured vapour pressures of LaF_3 by the torsion effusion method in the temperature range 1340–1650 K. There is apparently no doubt that the second law enthalpies from the various sources [4,16,17] are too inaccurate to be used in a meaningful discussion concerning the trend of the enthalpies of vaporization of the lanthanoid trifluorides. In the case of LuF_3 the only source to be compared with our results is the work of Zmbov and Margrave [5], who measured vapour pressures of LuF_3 by mass spectrometry in the temperature range 1250–1430 K. As far as the agreement between the second and third law data and the absence of a significant dependence of $\Delta_v H^\circ_{298}$(III) on temperature are concerned, our results are clearly closer to the true situation than those of [5]. It is therefore concluded that the difference between the third law enthalpies of vaporization of LaF_3 and LuF_3 derived in this work can be used to calculate the respective difference at 1500 K for both trifluorides in the liquid state, and hence can be related to the result of [3]. The only thermodynamic quantity which has to be estimated for this purpose is the enthalpy of fusion of LaF_3 at 1500 K.

$$\Delta_m H^\circ_T = \Delta_m H^\circ_{T_m} - \left\{\left[H^\circ_{T_m} - H^\circ_T\right](\mathrm{l}) - \left[H^\circ_{T_m} - H^\circ_T\right](\mathrm{s})\right\} \qquad (6)$$

In cases where the specific heats of the solid and the liquid phase are very similar at the melting point T_m, one can reliably assume that the enthalpy of fusion is practically independent of temperature within a reasonable temperature range. Unfortunately, this assumption cannot be made for LaF_3, because Δc_p equals 172.9 J mol^{-1} K^{-1} at $T_m = 1766$ K, with $\Delta_m H^\circ_{1766} = 50.2$ kJ mol^{-1} [6]. The enthalpy increment $[H^\circ_{1766} - H^\circ_{1500}]$ for LaF_3(l) can be estimated by extrapolation of the ΔH vs. T polynomial calculated in ref. 6 for the temperature range 1766–1873 K. This leads to $\Delta_m H^\circ_{1500} = 2.3$ kJ mol^{-1}, a result which discloses an extreme dependence of the enthalpy of melting on temperature. Although it is impossible to estimate reliably the accuracy of $\Delta_m H^\circ_{1500}$, this extrapolated value will be used to find $\Delta\Delta_v H^\circ_{1500}[LaF_3(l) - LuF_3(l)]$. All data necessary for the calculation are summarized in Table 5. The result, +25.1 kJ mol^{-1}, is in good agreement with the corresponding result of Gibson and Haire [3], +33 kJ mol^{-1}. This agreement allows us to conclude that thermochemical vaporization data derived from careful absolute vapour pressure measurements are quite comparable with results drawn from relative measurements of the type performed in [3]. It is finally worth emphasizing that $\Delta\Delta_v H^\circ_T$ changes sign on extrapolation from 1500 to 298 K. Because of the unusual similarity of the enthalpies of vaporization of the lanthanoid trifluorides, one should

TABLE 5

Data for the calculation of $\Delta\Delta_v H^\circ_{1500}[\mathrm{LaF_3(l)} - \mathrm{LuF_3(l)}]$ (kJ mol^{-1})

Compound	$H^\circ_{1500} - H^\circ_{298}$	$\Delta_m H^\circ_{1500}$ [a]	$\Delta_v H^\circ_{1500}$(III)	$\Delta_v H^\circ_{298}$(III)
LaF_3(s)	132.1	2.3	395.6	433.0
LaF_3(g)	97.0	–		
LuF_3(s, l)	179.0	–	370.5	453.2
LuF_3(g)	96.3			

[a] Estimated value (see text).

therefore refrain from assuming that a trend of the data observed for an elevated temperature will be retained on extrapolation to 298 K.

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