Articles

Thermodynamic Properties of the Rare Earth Element Vapor Complexes $LnAl_3Cl_{12}$ from Ln = La to Ln = Lu

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Received June 21, 1996[⊗]

Systematic analysis of rare earth element complexes has been carefully carried out in the liquid and solid states but not in the gaseous state because of the lack of a complete set of experimental data for any kind of vapor complexes of all rare earth elements. Here we present experimental quenching results which suggest that the $LnAl_3Cl_{12}$ complexes are the predominant vapor complexes roughly in the temperature range 588−851 K and pressure range 0.01−0.22 MPa for all of the 14 rare earth elements Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. For these elements, thermodynamic functions of the reactions $LnCl_3(s) + {}^3/_2Al_2Cl_6(g) = LnAl_3Cl_{12}(g)$ were calculated from the measurements. Those for the radioelement Pm were smoothly interpolated. The results show Gd divergences from the standard enthalpies and standard entropies from $LaAl_3Cl_{12}$ to $LuAl_3Cl_{12}$.

Introduction

Rare earth element complexes in liquid and solid states have been carefully investigated since the early 1950s. The experimental results often show anomalies such as Gd divergence,[1] tetrad,[2] double−double,[3] and inclined W effects.[4] Until now, however, a similar systematic analysis has not been carried out for rare earth element vapor complexes due to the lack of a complete set of experimental data for all of the rare earth elements.

Rare earth element complexes in the gaseous state are just as important as those in the condensed states. Rare earth element vapor complexes were recently studied in terms of various application possibilities such as laser materials,[5−8] luminescent materials for high-intensity discharge lamps,[9−11] and intermediate materials for preparation of anhydrous rare earth elements halides in high purities,[12−14] for mutual separation of rare earth elements[15−21] and for recovery of rare earth metals.[22,23] Moreover, unlike those in the condensed states, molecular interactions in the gaseous state could be neglected, which would make the vapor complexes model systems for studying the nature of the rare earth elements in their complexes.

Thermodynamic functions of the reactions $LnCl_3(s) + (n/2)Al_2Cl_6(g) = LnAl_nCl_{3n+3}(g)$ (where Ln = rare earth elements) have been determined for Ln = Nd with $n = 1$ by mass spectrometric measurements,[24] for Ln = Nd with $n = 3$[25] and $n = 4$[25] and for Ln = Sm with $n = 3$[26] by UV−vis spectrometric measurements, for Ln = Gd with $n = 3$ by entrainment, quenching, and chemical transport experiments,[27] and for Ln = Gd,[28] Tm,[28] and Yb[29] with $n = 1−4$ by radiochemical analysis. In all the cases, the $LnAl_3Cl_{12}$ complexes were found to be the predominant vapor complexes in the temperature range 500−900 K for Ln = Nd,[25] Sm,[26] Gd,[27,28] Tm,[28] and Yb.[29] However, Papatheodorou and Kucera[26] and Steidl et al.[28,29] noted that thermodynamic values of the $NdAl_3Cl_{12}$ complex reported by Øye and Gruen[25] were considerably different from those of $SmAl_3Cl_{12}$,[26] $GdAl_3Cl_{12}$,[28] $TmAl_3Cl_{12}$,[28] and $YbAl_3Cl_{12}$[29] reported by themselves.

We[30] carried out a thermodynamic study of the same reactions for Ln = Sc and Y at 588−806 K and 0.02−0.22 MPa by quenching experiments and found the $LnAl_2Cl_9$ complexes to be the predominant vapor complexes. We have tried to extend

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[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

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S0020-1669(96)00746-X CCC: $14.00

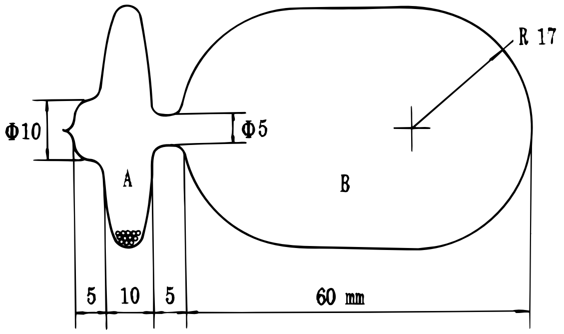

Figure 1. The ampule.

the present work to the $LnAl_3Cl_{12}$ complexes roughly in the ranges 588−851 K and 0.01−0.22 MPa for the 14 rare earth elements Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu to systematically study the thermodynamic properties of the vapor complexes $LnAl_3Cl_{12}$ from Ln = La to Ln = Lu.

Experimental Section

The chemicals used in this study were of 98.0% purity for anhydrous $AlCl_3$, 99.0% purity for anhydrous NH_4Cl, 99.95% purity for $CeCl_3\cdot 7H_2O$, and more than 99.9% purity for Pr_6O_{11}, Tb_4O_7, and Ln'_2O_3 (where Ln′ = La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, and Lu). Anhydrous $AlCl_3$ was further purified by careful sublimation under vacuum. The first two anhydrous rare earth element chlorides, $LaCl_3$ and $CeCl_3$, were prepared by reactions of La_2O_3 and $CeCl_3\cdot 7H_2O$, respectively, with a large excess of anhydrous NH_4Cl in an evacuated quartz tube at about 500−600 K. The residual NH_4Cl was removed by sublimation at 700 K under vacuum. The other 12 anhydrous rare earth element chlorides Ln^*Cl_3 (here Ln* = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) were prepared by the direct reaction of their corresponding oxides with a large excess of $AlCl_3$ at 573 K in evacuated and sealed quartz tubes. The quartz tubes were then subjected to a temperature gradient from 650 to 450 K, where the rare earth element chlorides Ln^*Cl_3 were chemically transported via their vapor complexes $Ln^*Al_nCl_{3n+3}$, which resulted in the deposition of Ln^*Cl_3 at the middle of the tubes. (The anhydrous $LaCl_3$ can also be prepared by this method.) This method was designed and reported by Papatheodorou and Kucera[26] for preparing $SmCl_3$ and other lanthanide and actinide halides and then used by Steidl et al.[28,29] for preparing $GdCl_3$, $TmCl_3$, and $YbCl_3$. The residual $AlCl_3$ coexisting with the rare earth element chlorides was removed by reheating the chlorides in cylindrical alumina tubes under a carrier gas consisting of dry Cl_2 and dry N_2.[15−21] All anhydrous chemicals were handled in a glovebox containing a dry argon atmosphere with a water vapor level less than 20 ppm.

The complexation equilibrium reactions were carried out in closed ampules made from Pyrex glass with a special shape as shown in Figure 1. This design was similar to those described in the literature.[27,30,31] An excess of $LnCl_3$ and less $AlCl_3$ were placed in the deep ditch of the ampule (see part A in Figure 1), and the ampule was then sealed under vaccum. Four ampules were placed in a graphite container and placed in a furnace, where the temperature was kept constant within ±0.5 K monitored with a $Pt-PtRu_{10}$ thermocouple; the maximum temperature difference in the container was always smaller than 1.0 K, so that all the samples were kept at the same temperature during each run. This design is similar to that used in our high-temperature thermodynamic measurements for alloys,[32−34] molten salt mixtures,[35,36] and slags.[37]

The literature showed that solid−liquid phases and solid solutions of $AlCl_3-LnCl_3$ might exist at temperatures lower than 577 K for $NdCl_3$,[25] 600 K for $SmCl_3$,[26] 550 K for $GdCl_3$[28] and $TmCl_3$,[28] and 500 K for $YbCl_3$,[29] where the activity of $LnCl_3$ is unknown. The literature[25,28,29] also showed that the predominant vapor complexes $LnAl_3Cl_{12}$ may coexist with the secondary complexes $LnAl_4Cl_{15}$, $LnAl_2Cl_9$, and $LnAlCl_6$ in a different temperature range of 500−900 K for different rare earth elements, in which case the equilibrium constants of the different complexes had to be calculated by using a complicated procedure,[27,28] resulting in additional errors. Moreover, our preliminary experiments showed that the samples reacted with Pyrex glass above 900 K and that the glass ampules broke easily during quenching with an equilibrium pressure of >0.25 MPa at high temperatures. On the other hand, the melting point of $TbCl_3$ is only 855 K. Thus, we chose suitable ranges of 588−851 K and 0.01−0.22 MPa for each of the 14 rare earth element complexes to ensure the complete evaporation of $AlCl_3$ and the existence of pure solid $LnCl_3$ in the deep ditches of the ampules and to avoid the formation of the secondary complexes, so that the activities of $LnCl_3(s)$ were always equal to unity and the equilibrium constants of the predominant vapor complexes $LnAl_3Cl_{12}$ could easily be determined. Preliminary experiments for the $AlCl_3-PrCl_3$ and $AlCl_3-HoCl_3$ systems at about 700 K showed that the complexation equilibria might be achieved within 5 h. Therefore, the formal equilibrium period was chosen to be 6 h for each run. After the thermodynamic equilibria had been achieved, the other ends of the ampules (part B in Figure 1) were quickly covered with asbestos and then quenched with water. Thus, the equilibrium gas phases were condensed and the mole numbers of Cl^- and Ln^{3+} in the condensates could then be determined by titration and spectrophotometry, respectively.

Results and Discussion

In all previous publications,[24−30] only the monolanthanide complexes $LnAl_nCl_{3n+3}$ were assumed to be formed; this means that $m = 1$ in $Ln_mAl_nCl_{3(m+n)}$. This assumption may reasonably be extended to Ln = La−Lu in this study. Thus, the complexation reactions may generally be expressed as

$$LnCl_3(s) + (n/2)Al_2Cl_6(g) = LnAl_nCl_{3n+3}(g) \qquad (1)$$

with the equilibrium constant

$$K_p = (p_{LnAl_nCl_{3n+3}}/p°)/(p_{Al_2Cl_6}/p°)^{n/2} \qquad (2)$$

where $p° = 0.100$ MPa. In the simplest case, where only one complex is formed, the values of n, K_p, $p_{Al_2Cl_6}$, and $p_{LnAl_nCl_{3n+3}}$ in eq 2 may be calculated by

$$\ln(p_{LnAl_nCl_{3n+3}}/p°) = \ln K_p + (n/2)\ln(p_{Al_2Cl_6}/p°) \qquad (3)$$

$$p_{LnAl_nCl_{3n+3}} = RTn_{LnAl_nCl_{3n+3}}/V \qquad (4)$$

$$p_{Al_2Cl_6} = RTn_{Al_2Cl_6}/V \qquad (5)$$

$$p_{AlCl_3} = RTn_{AlCl_3}/V \qquad (6)$$

$$n_{Ln^{3+}} = n_{LnAl_nCl_{3n+3}} \qquad (7)$$

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$$n_{\mathrm{Cl^-}} = 3n_{\mathrm{AlCl_3}} + 6n_{\mathrm{Al_2Cl_6}} + (3n+3)n_{\mathrm{LnAl}_n\mathrm{Cl}_{3n+3}} \tag{8}$$

and[24−30]

$$\log K'_{\mathrm{p,10}} = 2\log(p_{\mathrm{AlCl_3}}/p^{\circ\prime}) - \log(p_{\mathrm{Al_2Cl_6}}/p^{\circ\prime}) = 6.649 - 5.684 \times 10^3(1/T) - 1.607 \times 10^5(1/T)^2 \tag{9}$$

where T is the reaction temperature, V is the volume of the ampule, n_i and p_i are mole number and partial pressure of component i, and $K'_{\mathrm{p,10}}$ is the equilibrium constant of the dissociation reaction 10 with a special standard pressure of $p^{\circ\prime} =$ 0.101 325 MPa.

$$\mathrm{Al_2Cl_6(g)} = 2\mathrm{AlCl_3(g)} \tag{10}$$

The total pressure may be calculated by

$$P_\mathrm{T} = p_{\mathrm{AlCl_3}} + p_{\mathrm{Al_2Cl_6}} + p_{\mathrm{LnAl}_n\mathrm{Cl}_{3n+3}} \tag{11}$$

Here we only report the experimental results for each of the 14 rare earth elements in the temperature range where the $LnAl_3Cl_{12}$ complexes are predominant. Experimental results in other temperature ranges where $LnAl_3Cl_{12}$ coexist with $LnAl_4Cl_{15}$ or $LnAl_2Cl_9$ will be reported elsewhere.

The first four columns in Tables S1−S14 (Supporting Information) list the volumes of the ampules, total pressures, and partial pressures of Al_2Cl_6 and $LnAl_nCl_{3n+3}$, respectively, at every reaction temperature for the 14 rare earth elements. The fifth column lists the apparent values of the stoichiometric factor n determined by a least-squares computation in terms of eq 3. It can be seen that all the apparent values of n are 2.9−3.1 and are independent from temperature. Also, all the plots of $\ln(p_{\mathrm{LnAl}_n\mathrm{Cl}_{3n+3}}/p^\circ)$ vs $\ln(p_{\mathrm{Al_2Cl_6}}/p^\circ)$ are straight lines as shown in Figure S1 (Supporting Information). Both of these features meet the requirement of eq 3. Thus, $LnAl_3Cl_{12}$ are the predominant vapor complexes from Ln = La to Ln = Lu to a first approximation. The equilibrium constants for the $LnAl_3Cl_{12}$ vapor complexes from Ln = La to Ln = Lu could then be calculated by eq 2, and the results are listed in the last column of Tables S1−S14. Figure 2 shows the plots of $R \ln K_\mathrm{p}$ vs $1/T$ for the $LnAl_3Cl_{12}$ complexes of the 14 elements. It can be seen that all of them are also straight lines.

Let ΔG°, ΔH°, ΔS°, and ΔC_p° denote the molar Gibbs free energy, molar enthalpy, molar entropy, and molar heat capacity of reaction 1. One may then define ΔG°:

$$\Delta G^\circ = -RT \ln K_\mathrm{p} = \Delta H^\circ - T\Delta S^\circ \tag{12}$$

Previous publications assumed $\Delta C_p^\circ = 0$ J mol^{-1} K^{-1} for the vapor complexes $NdAl_3Cl_{12}$,[28,38] $SmAl_3Cl_{12}$,[28] $GdAl_3Cl_{12}$,[28] $TmAl_3Cl_{12}$[28], and $YbAl_3Cl_{12}$.[29] This assumption may reasonably be extended to the vapor complexes $LnAl_3Cl_{12}$ from Ln = La to Ln = Lu in this study. The molar enthalpies and molar entropies of reaction 1 for the vapor complexes $LnAl_3Cl_{12}$ of the 14 rare earth elements at 298 K can then be determined by a least-squares computation in terms of eq 12 and those of $PmAl_3Cl_{12}$ may then be smoothly interpolated in terms of atomic number of Ln^{3+}. All the results are listed in Table 1 and shown in Figures 3 and 4, respectively.

The probable overall errors of the ΔG°, ΔH°, and ΔS° values should be computed from the statistical errors and the estimated probable uncertainties.[39,40] The statistical errors calculated from the equilibrium constant data for $LnAl_3Cl_{12}$ from Ln = La to Ln = Lu are not more than ±0.2 kJ mol^{-1} for ΔG° at every temperature, ±0.7 kJ mol^{-1} for $\Delta H^\circ_{T_\mathrm{m}}$ and ±1.0 J mol^{-1} K^{-1} for $\Delta S^\circ_{T_\mathrm{m}}$, where the subscript T_m denotes mean experimental temperature. While the estimated probable uncertainties may arise from absolute errors of the chemical analysis for Ln^{3+} and Cl^- as ±0.5%, of the volume measurement of the ampule as ±0.5%, and of the temperature measurement as ±2.0 K, these uncertainties together with that inherent in eq 9 and the error from the scatter of the experimental points in Figures S1 and 2 may give rise to the probable overall errors of ±0.5 kJ mol^{-1} for ΔG°, ±1.5 kJ mol^{-1} for $\Delta H^\circ_{T_\mathrm{m}}$, and ±2.0 J mol^{-1} K^{-1} for $\Delta S^\circ_{T_\mathrm{m}}$ for $LnAl_3Cl_{12}$ from Ln = La to Ln = Lu, being the same as those for $ScAl_2Cl_9$ and YAl_2Cl_9.[30] Moreover, because no experimental data were available for the heat capacities of the vapor complexes, Schäfer[24,38] introduced the estimated values of $\Delta C_p^\circ = -12$ J mol^{-1} K^{-1} for $LnAlCl_6$, $\Delta C_p^\circ = 0$ J mol^{-1} K^{-1} for $LnAl_3Cl_{12}$, and $\Delta C_p^\circ = 14$ J mol^{-1} K^{-1} for $LnAl_4Cl_{15}$ and then Steidl et al.[28,29] introduced $\Delta C_p^\circ = -8$ J mol^{-1} K^{-1} for $LnAl_2Cl_9$. We[30] have assumed an absolute error of ±2.0 J mol^{-1} K^{-1} for the estimated value of $\Delta C_p^\circ = -8$ J mol^{-1} K^{-1} for $ScAl_2Cl_9$ and YAl_2Cl_9. Similarly, we may assume an absolute error of ±1.0 J mol^{-1} K^{-1} for the estimated value of $\Delta C_p^\circ = 0$ J mol^{-1} K^{-1} for $LnAl_3Cl_{12}$ from Ln = La to Ln = Lu, resulting in the additional probable uncertainties of not more than ±0.5 kJ mol^{-1} for $(\Delta H^\circ_{T_\mathrm{m}} - \Delta H^\circ_{298})$ and not more than ±1.0 J mol^{-1} K^{-1} for $(\Delta S^\circ_{T_\mathrm{m}} - \Delta S^\circ_{298})$. Therefore, the probable overall errors may be ±2 kJ mol^{-1} for ΔH°_{298} and ±3 J mol^{-1} K^{-1} for ΔS°_{298}, respectively, for $LnAl_3Cl_{12}$ from Ln = La to Ln = Lu.

The literature thermodynamic data for the $LnAl_3Cl_{12}$ complexes where Ln = Nd,[25] Sm,[26] Gd,[27,28] Tm,[28] and Yb[29] determined by using different methods mentioned above are also listed in Table 1, where only the $GdAl_3Cl_{12}$ data were determined previously by two research groups using different methods. It can be seen that the values of $\Delta H^\circ_{298} = 27.3$ kJ mol^{-1} and $\Delta S^\circ_{298} = -4.6$ J mol^{-1} K^{-1} for $SmAl_3Cl_{12}$ reported in this study exactly fit those of $\Delta H^\circ_{298} = 28.0$ kJ mol^{-1} and $\Delta S^\circ_{298} = -4.2$ J mol^{-1} K^{-1} reported by Papatheodorou and Kucera.[26] It can also be seen that the value of $\Delta H^\circ_{298} = 29.0$ kJ mol^{-1} for $GdAl_3Cl_{12}$ reported in this study is almost the same as that of $\Delta H^\circ_{298} = 30.7$ kJ mol^{-1} reported by Steidl et al.[28] and that the value of $\Delta S^\circ_{298} = 2.9$ J mol^{-1} K^{-1} for $GdAl_3Cl_{12}$ reported in this study is almost equal to the average values of both $\Delta S^\circ_{298} = 11$ J mol^{-1} K^{-1} reported by Cosandey and Emmenegger[27] and $\Delta S^\circ_{298} = -6.7$ J mol^{-1} K^{-1} reported by Steidl et al.[28] Our measurements also agree reasonably well with those for $TmAl_3Cl_{12}$ and $YbAl_3Cl_{12}$ determined by Steidl et al.[28,29] but not so well with those for $NdAl_3Cl_{12}$ determined by Øye and Gruen.[25] As mentioned above, Papatheodorou and Kucera[26] and Steidl et al.[28,29] have noted the considerable difference between their thermodynamic values for $SmAl_3Cl_{12}$, $GdAl_3Cl_{12}$, $TmAl_3Cl_{12}$, and $YbAl_3Cl_{12}$ and those for $NdAl_3Cl_{12}$ reported by Øye and Gruen.[25] Also, they[26] suggested that this difference might be attributed either to the experimental uncertainties of the methods used or to the different bondings and structures of the vapor complexes. However, the experiments showed that the overall adsorption spectrum for the vapor complexes $LnAl_3Cl_{12}$ was similar to those observed in con-

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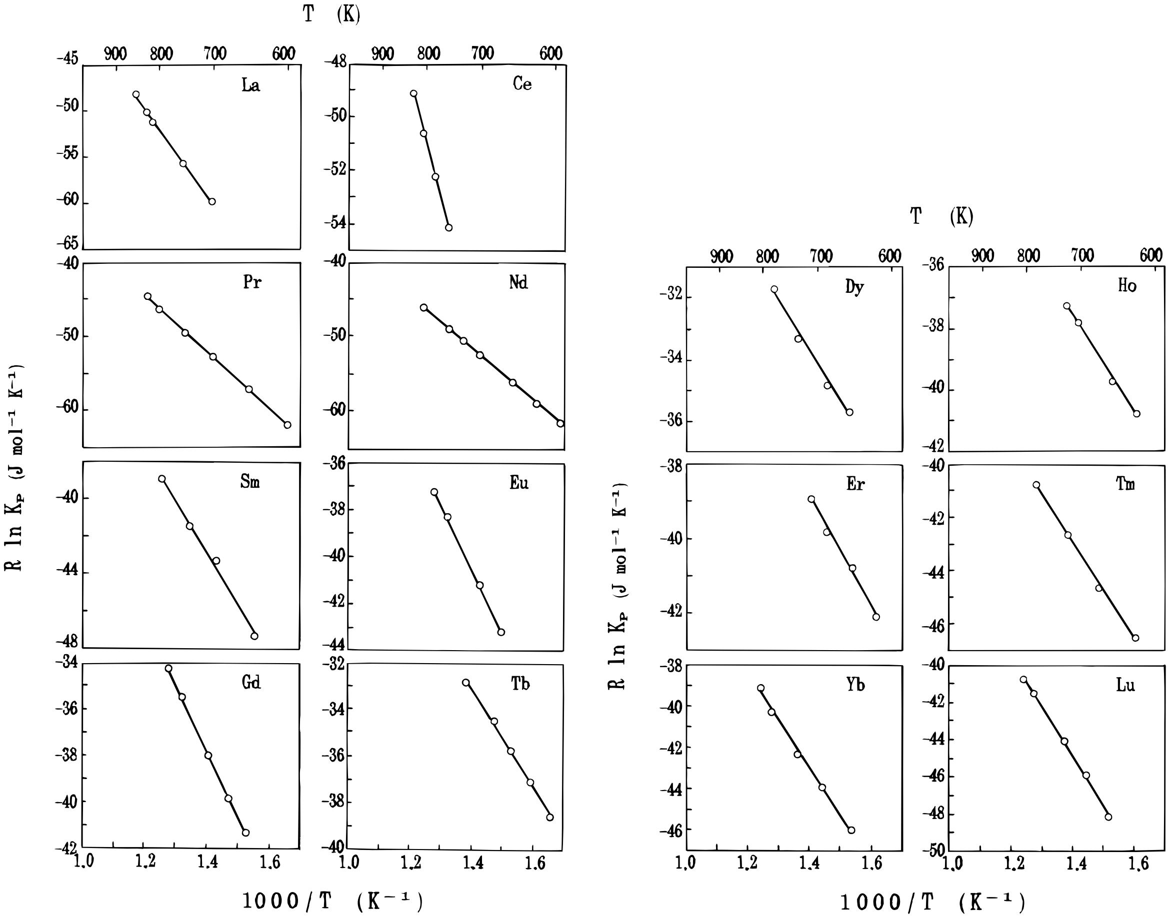

Figure 2. Plots of R ln K_p vs $1/T$ for the rare earth element vapor complexes $LnAl_3Cl_{12}$ from Ln = La to Ln = Lu; $p° = 0.100$ MPa.

Table 1. Thermodynamic Properties of the Reactions $LnCl_3(s) + (n/2)Al_2Cl_6(g) = LnAl_nCl_{3n+3}(g)$

	$\Delta H°_{298}$, kJ mol^{-1}	$\Delta S°_{298}$, J mol^{-1} K^{-1}	ref
La	47.9 ± 2	7.8 ± 3	this study
Ce	43.6 ± 2	3.6 ± 3	this study
Pr	38.2 ± 2	1.2 ± 3	this study
Nd	34.6 ± 2	−3.3 ± 3	this study
	45.2 ± 1	8.4 ± 1	25
Pm	30.6 ± 2[a]	−4.0 ± 3[a]	this study
Sm	27.3 ± 2	−4.6 ± 3	this study
	28.0 ± 0.8	−4.2 ± 0.8	26
Eu	23.5 ± 2	−6.3 ± 3	this study
Gd	29.0 ± 2	2.9 ± 3	this study
	35.8 ± 8	11.0 ± 11	27
	30.7 ± 4	−6.7 ± 8	28
Tb	21.1 ± 2	−3.5 ± 3	this study
Dy	16.6 ± 2	−10.5 ± 3	this study
Ho	16.1 ± 2	−14.9 ± 3	this study
Er	14.8 ± 2	−18.2 ± 3	this study
Tm	18.0 ± 2	−16.7 ± 3	this study
	27.7 ± 4	−9.6 ± 8	28
Yb	22.7 ± 2	−11.1 ± 3	this study
	27.6 ± 4	−11.5 ± 8	29
Lu	26.7 ± 2	−7.4 ± 3	this study

[a] Interpolated values.

densed states for each trivalent lanthanide[41] and that the solid molecules $DyAl_3Cl_{12}$,[13] $HoAl_3Cl_{12}$,[42] $LaAl_3Br_{12}$,[14] $PrAl_3Br_{12}$,[14] and $NdAl_3Br_{12}$[14] all possessed trigonal symmetry, which would unlikely support the second argument. Furthermore, the thermodynamic values for $NdAl_3Cl_{12}$ are $\Delta G°_{800} = 36.8$ kJ mol^{-1} and $\Delta G°_{600} = 38.9$ kJ mol^{-1} derived from ref 25, while $\Delta G°_{800} = 37.2$ kJ mol^{-1} and $\Delta G°_{600} = 36.6$ kJ mol^{-1} derived from this paper. Both only show a larger difference at low temperature where a lower pressure ratio of the complex to aluminum chloride may make the spectroscopic investigation rather difficult.[41] Therefore, the experimental uncertainties for $NdAl_3Cl_{12}$ at low temperature in ref 25 might be the main cause for the difference in the thermodynamic data reported by Øye and Gruen[25] and those reported by all the others.

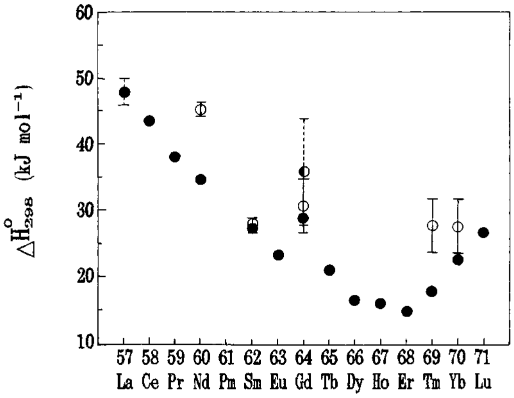

Figure 3. Series behavior of $\Delta H°_{298}$ for the vapor complexes $LnAl_3Cl_{12}$ from Ln = La to Ln = Lu: ●, this study; ○ and ◐, literature data.[25−29] The probable overall error of $\Delta H°_{298}$ reported in this study for each of the 14 elements is ±2 kJ mol^{-1} (only shown at Ln = La), while those reported in the literature are different for Ln = Nd,[25] Sm,[26] Gd,[27,28] Tm,[28] and Yb.[29]

This study reports the first complete set of property values for the rare earth element vapor complexes from Ln = La to Ln = Lu. As shown in Figures 3 and 4, the values of $\Delta H°_{298}$ and $\Delta S°_{298}$ for the $LnAl_3Cl_{12}$ complex decrease from Ln = La

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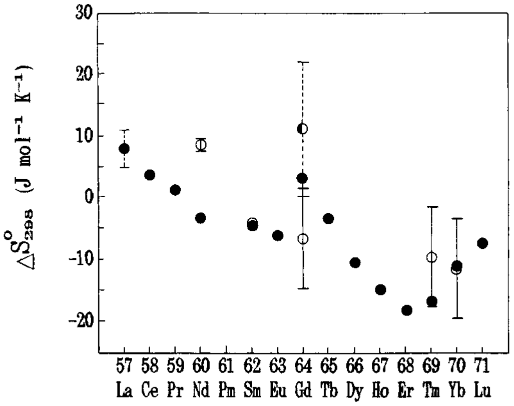

Figure 4. Series behavior of ΔS°_{298} for the vapor complexes $LnAl_3Cl_{12}$ from Ln = La to Ln = Lu: ●, this study; ○ and ◐, literature data.[25−29] The probable overall error of ΔS°_{298} reported in this study for each of the 14 elements is ±3 J mol^{-1} K^{-1} (only shown at Ln = La), while those reported in the literature are different for Ln = Nd,[25] Sm,[26] Gd,[27,28] Tm,[28] and Yb.[29]

to Ln = Eu and then increase from Ln = Eu to Ln = Gd in the left-hand sides and decrease from Ln = Gd to Ln = Er and then increase from Ln = Er to Ln = Lu in the right-hand sides, indicating a significant Gd divergence and two weak minimum points at Ln = Eu and Er. Here the Gd divergence is consistent with the half-filled 4f shell. Moreover, our previous paper[30] and this paper suggest that the predominant vapor complexes are $LnAl_2Cl_9$ for Ln = Sc and Y but $LnAl_3Cl_{12}$ from Ln = La to Ln = Lu in roughly the same temperature and pressure ranges (i.e., 500−800 K and 0.01−0.22 MPa). Sc^{3+} is the smallest rare earth element trivalent ion but Y^{3+} is at least larger than Tm^{3+}, Yb^{3+}, and Lu^{3+}. Therefore, the rare earth element ionic radii are not decisive factors for the stoichiometry of the predominant vapor complexes $LnAl_nCl_{3n+3}$. On the other hand, up to now scientists have had different opinions on the nature of the rare earth element complexes even in the condensed states. The Gd divergence effect in the rare earth element liquid complexes, for example, has been explained by a change either in the 4f electron configuration or in the coordination number.[43] Similar to the second explanation, Papatheodorou[26,41] assumed a 9-fold coordination structure for early lanthanides and a near-octahedral coordination structure for end lanthanides in the $LnAl_3Cl_{12}$ vapor complexes. However, recent experiments found the same microstructure for the solid complexes $DyAl_3Cl_{12}$,[13] $HoAl_3Cl_{12}$,[42] $LaAl_3Br_{12}$,[14] $PrAl_3Br_{12}$,[14] and $NdAl_3Br_{12}$.[14] Moreover, both Sc^{3+} and Y^{3+} have no 4f electrons. In general, La^{3+} is also believed to have no 4f electrons. However, Gschneidner[44] recently assumed La^{3+} to have 4f electron hybridization and explained physical and chemical properties of pure metals, compounds, alloys, and EDTA complexes in aqueous solutions of rare earth elements by using 4f hybridization. It would seem that the 4f hybridization concept is supported by the recent theoretical calculation of Temmerman et al.,[45] who found the unoccupied 4f bands in Pr metal to hybridize strongly with the conduction s, p, and d bands. Therefore, 4f hybridization might be accepted as a reasonable explanation both for the difference in the stoichiometry of the predominant vapor complexes $LnAl_2Cl_9$ for Ln = Sc and Y and $LnAl_3Cl_{12}$ from Ln = La to Ln = Lu and for the Gd divergence from the behavior of the vapor complexes $LnAl_3Cl_{12}$ from Ln = La to Ln = Lu if the same calculation results and direct experimental evidence on the microstructure of Ln = La can be obtained. Until now, however, the 4f hybridization concept has not been accepted by many scientists, as pointed out by Gschneidner himself.[46] One of the reviewers suggested that a structure change in the gas phase of the $LnAl_3Cl_{12}$ molecules for the heavier lanthanides might be responsible for the differences between the results for Sc^{3+} and Y^{3+}, on the one hand, and the results for Tm^{3+}, Yb^{3+}, and Lu^{3+}, on the other. Therefore, further experimental and theoretical studies on the microstructures of the vapor complexes $LnAl_nCl_{3n+3}$ will be very interesting and will provide a more satisfactory understanding of the mechanisms of the systematics and anomalies in their thermodynamic properties from Ln = Sc to Ln = Lu.

Acknowledgment. This work was supported by the National Natural Science Foundation of China and partly supported by the Doctoral Foundation of the State Educational Committee. The publication costs of this paper were absorbed by the Jin Shu-Liang Commemoration Fund of NU. We thank Y. Su and R.-J. Gao for assistance with the quenching experiments.

Supporting Information Available: Tables S1−S14, listing experimental quenching data for the vapor complexes $LnAl_nCl_{3n+3}$ of the 14 rare earth elements Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, and Figure S1, showing plots of $\ln(p_{LnAl_nCl_{3n+3}}/p^\circ)$ vs $\ln(p_{Al_2Cl_6}/p^\circ)$ for the same 14 rare earth elements (24 pages). Ordering information is given on any current masthead page.

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