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Systematics and Anomalies in Rare Earth/Aluminum Bromide Vapor Complexes: Thermodynamic Properties of the Vapor Complexes LnAl$_3$Br$_{12}$ from Ln = Sc to Ln = Lu

Zhi-Chang Wang*,† and Jin Yu†,‡

Department of Chemistry, Northeastern University, 3-11 Culture Road, Shenyang 110004, China, and School of Sciences, Shenyang University of Technology, 1 S. 13th Road, Shenyang 110023, China

Systematics and anomalies in the rare earth/aluminum bromide vapor complexes have been investigated by the phase equilibrium-quenching experiments. The measurements suggest that the LnAl$_3$Br$_{12}$ complexes are the predominant vapor complexes for the 16 rare earth elements Ln = Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu in the temperature range 601−833 K and pressure range 0.01−0.22 MPa, which is different from the rare earth/aluminum chloride systems, where the predominant vapor complexes are LnAl$_3$Cl$_{12}$ from Ln = La to Ln = Lu, but LnAl$_2$Cl$_9$ for Ln = Sc and Y are roughly in the same ranges, which indicates the importance of the halogen anion radius on the rare earth vapor complex formation. In the temperature and pressure ranges, gaseous Al$_2$Br$_6$ and AlBr$_3$ are dominant species and the molar fraction of LnAl$_3$Br$_{12}$ is normally less than 0.01. Thermodynamic functions of the reactions LnBr$_3$(s) + (3/2)Al$_2$Br$_6$(g) = LnAl$_3$Br$_{12}$(g) were calculated from the measurements for the 16 rare earth elements and then smoothly interpolated for the radioelement Ln = Pm. The standard molar enthalpies and standard molar entropies show significant Gd divergences from LaAl$_3$Br$_{12}$ to LuAl$_3$Br$_{12}$ when plotted as functions of the rare earth atomic number. They also suggest nearly linear manner for ScAl$_3$Br$_{12}$, LuAl$_3$Br$_{12}$, YAl$_3$Br$_{12}$, and LaAl$_3$Br$_{12}$ when plotted as functions of the rare earth ionic radius.

Introduction

Rare earth element complexes are of fundamental importance not only in the liquid and solid states but also in the gaseous state. In recent years there has been increased emphasis on the experimental and theoretical investigations of the rare earth element halide vapor complexes, particularly in the LnX$_3$−MX and LnX$_3$−AlX$_3$ systems (where Ln = rare earth, M = alkali metal, and X = halogen).[1−10] These complexes may enhance the volatility of the rare earth halides to 10^2 times in the former case and to 10^{13} times in the latter case. Therefore, they have been used as key constituents chemically transported in high-intensity discharge lamps, anhydrous rare earth halides production, and rare earth extraction and separation (see, for example, refs 1−3 and references therein). They may also act as better model systems than the liquid and solid complexes for understanding the nature of rare earth elements in their complexes because of the negligible molecular interactions at the gaseous state. Until now, however, experimental information is very limited on the systematics and anomalies in the thermodynamic properties of the rare earth element halide vapor complexes.

Thermodynamic properties of the reactions LnX$_3$(s) + (n/2)Al$_2$X$_6$(g) = LnAl$_n$X$_{3n+3}$(g) in the LnX$_3$−AlX$_3$ systems have been experimentally determined by the methods of

* To whom correspondence should be addressed. E-mail: wangzc@mail.neu.edu.cn.
† Northeastern University.
‡ Shenyang University of Technology.
(1) Boghosian, S.; Papatheodorou, G. N. Halide Vapors and Vapor Complexes. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Jr., Eyring, L., Eds.; Elsevier: Amsterdam, 1996; Vol. 23, p 435.
(2) Jiang, J.; Ozaki, T.; Machida, K.; Adachi, G. *J. Alloys Compd.* **1997**, *260*, 222.
(3) Oppermann, H.; Schmidt, P. *Z. Anorg. Allg. Chem.* **2005**, *631*, 1309.
(4) Hilpert, K.; Niemann, U. *Thermochim. Acta* **1997**, *299*, 49.
(5) Lisek, I.; Kapala, J.; Miller, M. *J. Alloys Compd.* **1998**, *280*, 77.
(6) Kapala, J.; Lisek, I.; Roszak, S.; Miller, M. *Polyhedron* **1999**, *18*, 2845.
(7) Akdeniz, Z.; Önem, Z. C.; Tosi, M. P. *Z. Naturforch.* **2001**, *56a*, 721.
(8) Önem, Z. C.; Akdeniz, Z.; Tosi, M. P. *Z. Naturforch.* **2002**, *57a*, 937.
(9) Groen, C. P.; Oskam, A.; Kovács, A. *Inorg. Chem.* **2000**, *39*, 6001.
(10) Groen, C. P.; Oskam, A.; Kovács, A. *Inorg. Chem.* **2003**, *42*, 851.

UV−vis spectrometry,[11−14] mass spectrometry,[15] radiochemistry,[16,17] quenching,[18−22] entrainment,[18] and chemical vapor transport.[23−28] Standard molar enthalpies and standard molar entropies of the reactions have been derived from the measurements for the chloride vapor complexes $LnAl_nCl_{3n+3}$ of the 16 rare earth elements Ln = Sc,[15,19] Y,[19,24] La,[21,22,27] Ce,[21,22] Pr,[21] Nd,[11,21,26] Sm,[12,21] Eu,[21,23] Gd,[16,18,21] Tb,[21] Dy,[20,21] Ho,[13,21,22] Er,[21] Tm,[16,21] Yb,[17,21] and Lu[21] and interpolated for that of the radioelement Ln = Pm.[21] However, the standard thermodynamic property values are available only for the bromide vapor complexes $LnAl_nBr_{3n+3}$ of Ln = Y[25] and La[28] and for the iodide vapor complexes $LnAl_nI_{3n+3}$ of Ln = Nd.[14] These results have recently been discussed in the excellent reviews of Boghosian and Papatheodorou,[1] Adachi and co-workers,[2] and Oppermann and Schmidt.[3] However, the chemical vapor transport data have not been collected in ref 2 and have only been denoted as estimated values in ref 1 probably due to the relatively large experimental uncertainties.

We[19−22] have improved the phase equilibrium-quenching technique and applied it to determine the stoichiometry and thermodynamic properties of the reactions $LnCl_3(s) + (n/2)Al_2Cl_6(g) = LnAl_nCl_{3n+3}(g)$ for the 16 rare earth elements Ln = Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, and the results agree well with most of the literature data. In this study, we extend the phase equilibrium-quenching investigations to the reactions $LnBr_3(s) + (n/2)Al_2Br_6(g) = LnAl_nBr_{3n+3}(g)$ for the 16 rare earth elements Ln = Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. We are interested in whether the systematics and anomalies in the $LnAl_nBr_{3n+3}$ vapor complexes are the same as those in the $LnAl_nCl_{3n+3}$ vapor complexes.

Experimental Section

The chemicals used in this study were of 99.999% purity for Al powder, more than 99.5% purity for Br_2, more than 99.99% purity
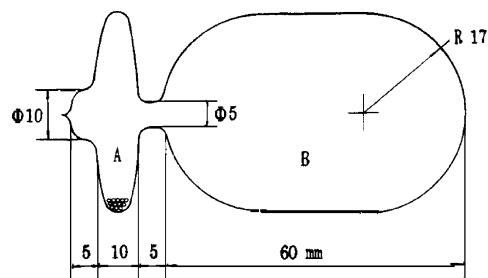

Figure 1. The ampule.

for $AlBr_3$, and more than 99.9% purity for CeO_2, Pr_6O_{11}, Tb_4O_7, and $Ln^*_2O_3$ (where Ln^* = Sc, Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, and Lu).

The anhydrous rare earth element bromides were prepared by the direct reactions of their corresponding oxides with a large excess of $AlBr_3$ at an atomic ratio Ln:Al =1:4. The main reactions may be expressed as $(1/2)Ln^*_2O_3(s) + (1/2)Al_2Br_6(g) = Ln^*Br_3(s) + (1/2)Al_2O_3(s)$, $CeO_2(s) + (1/2)Al_2Br_6(g) = CeBr_3(s) + (1/2)Al_2O_3(s) + (1/4)O_2(g)$, $(1/6)Pr_6O_{11}(s) + (1/2)Al_2Br_6(g) = PrBr_3(s) + (1/2)Al_2O_3(s) + (1/6)O_2(g)$, and $(1/4)Tb_4O_7(s) + (1/2)Al_2Br_6(g) = TbBr_3(s) + (1/2)Al_2O_3(s) + (1/8)O_2(g)$, respectively, where the latter three reactions produced oxygen, which may completely be removed by adding a small amount of Al powder. In a typical reaction, after placement of either 0.2 g of $Ln^*_2O_3$ and 1.2 g of $AlBr_3$ or 0.2 g of CeO_2, Pr_6O_{11}, or Tb_4O_7, 1.2 g of $AlBr_3$, and 0.015 g of Al powder into an one-end sealed quartz tube, 20 mm in inner diameter and 300 mm in length, under Ar atmosphere, and the sealing of its other end under vacuum, the reaction mixture was heated at 600 K for 1 h. The resultant $LnBr_3$ was separated from the crude product by the chemical vapor transport method. For doing so, the evacuated and sealed quartz tube was placed in a tubular furnace with a reduced temperature gradient from 750 to 460 K and the solid crude product was placed at the hot end of the quartz tube. Each of the chemical vapor transport reactions was carried out for 6 h. During the reactions, the vapor complexes $LnAl_nBr_{3n+3}$ were produced by the reactions of $LnBr_3$ with the residual $AlBr_3$ at the hot end of the quartz tube, chemically transported from the hot end to the cold end, and then decomposed into $LnBr_3(s)$ and $Al_2Br_6(g)$ at the cold end. After the reaction, the quartz tube was removed out quickly from the furnace and its hot end was quenched with water, where $AlBr_3$ was quickly condensed. By using this method, $LnBr_3$ may easily be separated from the residual reactors and other resultants. In addition, the anhydrous rare earth element bromides can also be prepared by dropping liquid Br_2 directly into a solid mixture consisting of the corresponding rare earth oxides and a large excess of Al powder in one-end sealed quartz tubes under Ar atmosphere and then chemically transported via their vapor complexes in the evacuated and sealed quartz tubes. All anhydrous chemicals were handled in a glovebox containing a dry argon atmosphere with a water vapor level less than 20 ppm.

The phase equilibrium-quenching experiments were carried out in closed ampules made from Pyrex glass with a special shape as shown in Figure 1. Less $AlBr_3$ and an excess of $LnBr_3$ were placed in the deep ditch of the ampule (part A in Figure 1), and the ampule was then sealed under vacuum. That may ensure $AlBr_3$ to evaporate completely and to react with part of the $LnBr_3(s)$ to reach an equilibrium at high temperature among $LnBr_3(s)$, $Al_2Br_6(g)$, and $LnAl_nBr_{3n+3}(g)$ in each ampule.

Four ampules were placed in a graphite container and then placed in a furnace, where the temperature was kept constant within ±0.5 K measured with a Pt−PtRh_{10} thermocouple. Preliminary experiments showed that the maximum temperature difference in the

(11) Øye, H. A.; Gruen, M. *J. Am. Chem. Soc.* **1969**, *91*, 2229.
(12) Papatheodorou, G. N.; Kucera, G. H. *Inorg. Chem.* **1979**, *18*, 385.
(13) Hoekstra, H. R.; Hessler, J. P.; Williams, C. W.; Carnall, W. T. In *High Temperature Metal Halide Chemistry*; Hildenbrand, D. L., Cubicciotti, D. D., Eds.; The Electrochenical Society: Pennington, NJ, 1978; PV 78-1, p 123.
(14) Kulset, N. High Temperature Study of Noedymium Halide Gas Complexes. Ph.D. Thesis, University of Trondheim, Trondheim, Norway, 1986.
(15) Schäfer, H.; Flörke, U. *Z. Anorg. Allg. Chem.* **1981**, *479*, 89.
(16) Steidl, G.; Bächmann, K.; Dienstbach, F. *J. Phys. Chem.* **1983**, *87*, 5010.
(17) Steidl, G.; Bächmann, K.; Dienstbach, F. *Polyhedron* **1983**, *2*, 727.
(18) Cosandey, M.; Emmenegger, F. P. *J. Electrochem. Soc.* **1979**, *126*, 1601.
(19) Wang, Z.-C.; Wang, L.-S.; Gao, R.-J.; Su, Y. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1887.
(20) Wang, L.-S.; Gao, R.-J.; Su, Y.; Wang, Z.-C. *J. Chem. Thermodyn.* **1996**, *28*, 1093.
(21) Wang, Z.-C.; Wang, L.-S. *Inorg. Chem.* **1997**, *36*, 1536.
(22) Wang, Z.-C.; Wang, L.-S. *J. Alloys Compd.* **1998**, *265*, 153.
(23) Lange, F. Th.; Bärnighausen, H. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1747.
(24) Oppermann, H.; Huong, D. Q. *Z. Anorg. Allg. Chem.* **1995**, *621*, 659.
(25) Oppermann, H.; Hennig, Z.; Dao Quoc, H. *Z. Naturforch.* **1998**, *53b*, 361.
(26) Oppermann, H.; Zhang, M.; Hennig, Z. *Z. Naturforch.* **1998**, *53b*, 1343.
(27) Oppermann, H.; Dao Quoc, H.; Morgenstern, A. *Z. Naturforch.* **1999**, *54b*, 1410.
(28) Oppermann, H.; Dao Quoc, H.; Zhang-Presse, M. *Z. Naturforch.* **2001**, *56b*, 908.

container was always smaller than 1.0 K, so that the four samples were kept at the same temperature during each run. The equilibrium period was 6 h for each run, which is the same as that for the rare earth element chloride complexes.[19−22] After the thermodynamic equilibrium 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 phase was quickly condensed in part B of the ampules and the mole numbers of Ln^{3+} and Br^- in the condensates could then be determined by spectrophotometry and titration, respectively. The equilibrium experiments were kept in the ranges 601−833 K and 0.01−0.22 MPa to avoid the high-temperature reaction between the bromides and Pyrex glass, the low-temperature formation of solid solutions or solid−liquid phases, and the glass ampule broken when quenching at high pressure.

Results and Discussion

1. Stoichiometry and Equilibrium Constants. In all previous publications,[11−28] only the mono-rare-earth vapor complexes $LnAl_nX_{3n+3}$ were assumed to be formed in the $LnX_3−AlX_3$ systems (i.e., $m = 1$ in $Ln_mAl_nX_{3(m+n)}$). Thus, the complexation reactions investigated in this study may be expressed as

$$LnBr_3(s) + (n/2)Al_2Br_6(g) = LnAl_nBr_{3n+3}(g) \quad (1)$$
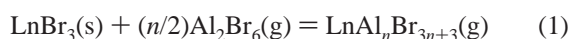
with the equilibrium constant

$$K_p = (p_{LnAl_nBr_{3n+3}}/p°)/(p_{Al_2Br_6}/p°)^{n/2} \quad (2)$$

where $p° = 0.100$ MPa. In the simple case that only one complex is formed, the values of n, K_P, $p_{Al_2Br_6}$, and $p_{LnAl_nBr_{3n+3}}$ in eq 2 may be calculated by

$$\ln(p_{LnAl_nBr_{3n+3}}/p°) = \ln K_p + (n/2) \ln(p_{Al_2Br_6}/p°) \quad (3)$$

$$p_{LnAl_nBr_{3n+3}} = RTn_{LnAl_nBr_{3n+3}}/V \quad (4)$$

$$p_{Al_2Br_6} = RTn_{Al_2Br_6}/V \quad (5)$$

$$p_{AlBr_3} = RTn_{AlBr_3}/V \quad (6)$$

$$n_{Ln^{3+}} = n_{LnAl_nBr_{3n+3}} \quad (7)$$

$$n_{Br^-} = 3n_{AlBr_3} + 6n_{Al_2Br_6} + (3n + 3)n_{LnAl_nBr_{3n+3}} \quad (8)$$

and[29]

$$\log K_{p,(10)} = 2 \log(p_{AlBr_3}/p°) - \log(p_{Al_2Br_6}/p°) = -2.647 +$$
$$4.149 \times \log T - 5.512 \times 10^3(1/T) - 3.752 \times 10^4(1/T)^2 -$$
$$3.745 \times 10^{-3} \times T + 9.295 \times 10^{-7} \times T^2 \quad (9)$$

where T is reaction temperature, V is volume of the ampule, n_i and p_i are the mole number and pressure of the component

(29) Barin, I. *Thermochemical Data of Pure Substances*, 3rd ed.; Wiley-VCH: Weinheim, Germany, 1995.

i, and $K_{p,(10)}$ is the equilibrium constant of the dissociation reaction 10

$$Al_2Br_6(g) = 2AlBr_3(g) \quad (10)$$
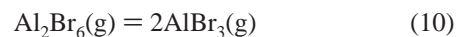
The total pressure may then be calculated by

$$P_{total} = p_{AlBr_3} + p_{Al_2Br_6} + p_{LnAl_nBr_{3n+3}} \quad (11)$$

In Tables Sl−S16 (Supporting Information) are listed the volumes of the ampules, total pressures, and partial pressures of Al_2Br_6 and $LnAl_nBr_{3n+3}$ at every reaction temperature for the 16 rare earth elements calculated by eqs 4−9 and 11. It can be seen that in the reactions gaseous Al_2Br_6 and $AlBr_3$ are dominant species and the molar fraction of $LnAl_3Br_{12}$ is normally less than 0.01. By a least-squares computation in terms of eq 3, the apparent values of the stoichiometric factor n may be calculated for $LnAl_nBr_{3n+3}$ for the 16 rare earth elements at different temperatures, and the results are also listed in Tables Sl−S16, which are all within 2.96−3.04 and independent of temperature. In Figure S1 (Supporting Information) are shown the plots of $\ln(p_{LnAl_nBr_{3n+3}}/p°)$ vs $\ln(p_{Al_2Br_6}/p°)$ of the 16 rare earth elements at different temperatures, which are all straight lines. These results can meet the requirement of eqs 3, 7, and 8. Thus, the $LnAl_3Br_{12}$ complexes are the predominant vapor complexes of the 16 rare earth elements to a first approximation. The equilibrium constants for the complexes $LnAl_3Br_{12}$ of the 16 rare earth elements can then be calculated by eq 3, and the results are listed in the last columns of Tables Sl−S16 (Supporting Information).

This study shows that the $LnAl_3Br_{12}$ complexes are the predominant vapor complexes from Ln = Sc to Ln = Lu in the ranges 601−833 K and 0.01−0.22 MPa. On the other hand, our previous papers[19,21] suggested the predominant vapor complexes to be $LnAl_3Cl_{12}$ from Ln = La to Ln = Lu but $LnAl_2Cl_9$ for Ln = Sc and Ln = Y in roughly the same temperature and pressure ranges. This indicates that the vapor complexes $ScAl_3X_{12}$ and YAl_3X_{12} are much more stable than $ScAl_2X_9$ and YAl_2X_9 for X = Br but reverse for X = Cl in the nearly the same reaction conditions. Therefore, the halogen ionic radius is the decisive factor for the stoichiometry of the predominant vapor complexes $ScAl_nX_{3n+3}$ and YAl_nX_{3n+3} for X = Cl and Br.

2. Standard Thermodynamic Quantities. Previous publications[11−18,20−23] assumed the molar heat capacity $\Delta C_P°$ = 0 J mol^{-1} K^{-1} for the reactions $LnCl_3(s) + (3/2)Al_2Cl_6(g)$ = $LnAl_3Cl_{12}(g)$ from Ln = La to Ln = Lu. This assumption may reasonably be extended to the reaction 1 for $LnAl_3Br_{12}$ from Ln = Sc to Ln = Lu in this study. Let $\Delta G°$, $\Delta H°$, and $\Delta S°$ denote the molar Gibbs free energy, molar enthalpy, and molar entropy of reaction 1, which are related by

$$\Delta G° = -RT \ln K_p = \Delta H° - T\Delta S° \quad (12)$$

As shown in Figure 2, plots of $R \ln K_p$ vs $1/T$ for the vapor complexes $LnAl_3Br_{12}$ of the 16 rare earth elements are all straight lines. The standard molar enthalpy and standard molar entropy of reaction 1 for $LnAl_3Br_{12}$ of the 16 rare earth
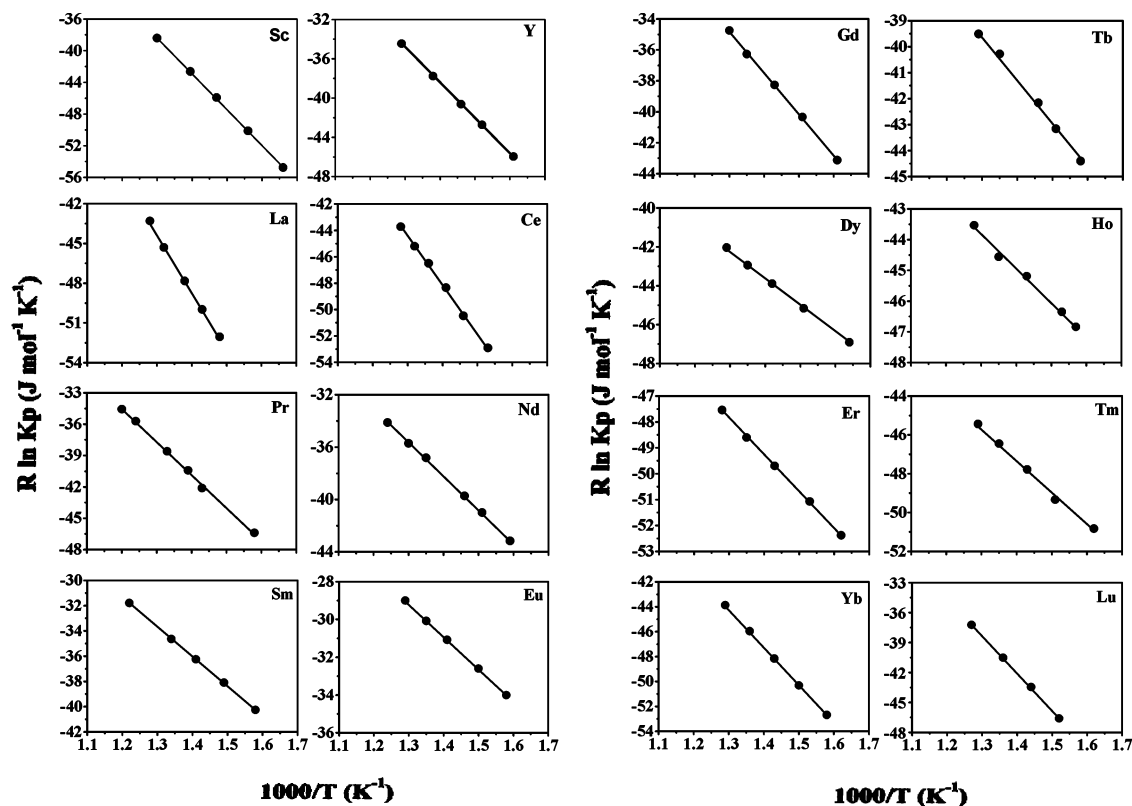
Figure 2. Plots of $R \ln K_p$ vs $1/T$ for the rare earth element vapor complexes $LnAl_3Br_{12}$ from Ln = Sc to Ln = Lu ($p° = 0.100$ MPa).

Table I. Thermodynamic Properties of the Complexation Reactions $LnBr_3(s) + (3/2)Al_2Br_6(g) = LnAl_3Br_{12}(g)$ from Ln = Sc to Ln = Lu

| atom	$\Delta H°_{298}$, kJ mol⁻¹	$\Delta S°_{298}$, J mol⁻¹ K⁻¹	ref
Sc	45.0 ± 2	20.2 ± 3	this study
Y	37.7 ± 2	14.5 ± 3	this study
	224 ± 8	217 ± 8	25[a]
La	42.8 ± 2	11.4 ± 3	this study
	21 ± 8	-8 ± 8	3, 28[a]
Ce	36.5 ± 2	3.0 ± 3	this study
Pr	31.2 ± 2	2.8 ± 3	this study
Nd	25.9 ± 2	-1.9 ± 3	this study
Pm	23.4 ± 2[b]	-2.9 ± 3[b]	this study
Sm	22.8 ± 2	-4.1 ± 3	this study
Eu	17.6 ± 2	-6.2 ± 3	this study
Gd	26.4 ± 2	-0.7 ± 3	this study
Tb	16.8 ± 2	-17.7 ± 3	this study
Dy	13.8 ± 2	-24.2 ± 3	this study
Ho	10.8 ± 2	-29.8 ± 3	this study
Er	13.7 ± 2	-30.2 ± 3	this study
Tm	16.5 ± 2	-24.3 ± 3	this study
Yb	29.7 ± 2	-5.6 ± 3	this study
Lu	37.0 ± 2	9.8 ± 3	this study

[a] Chemical vapor transport measurements. [b] Interpolated values.

elements at 298 K can then be determined by a least-squares computation in terms of eq 12, and those for $PmAl_3Br_{12}$ may be smoothly interpolated in terms of the rare earth element atomic number from Ln = La to Ln = Lu. All the results are listed in Table 1 and shown in Figures 3 and 4, respectively.

Similar to the $LnAl_3Cl_{12}$ vapor complexes,[21] the probable overall errors of the thermodynamic values for the $LnAl_3Br_{12}$ vapor complexes may be estimated by the following method. The absolute errors may be $\pm 0.5\%$ in the chemical analysis for Ln^{3+} and Br^-, $\pm 0.5\%$ in the volume measurement of the reaction ampule, and ± 2.0 K in the temperature
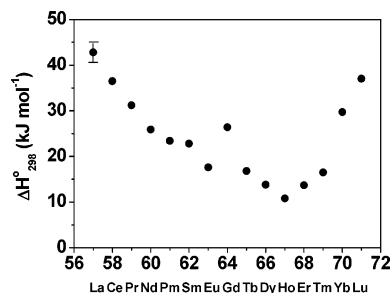
Figure 3. Atomic number dependence of the molar standard enthalpies for the rare earth element vapor complexes $LnAl_3Br_{12}$ from Ln = La to Ln = Lu reported in this study with the probable overall error ± 2 kJ mol⁻¹ (only shown at Ln = La).
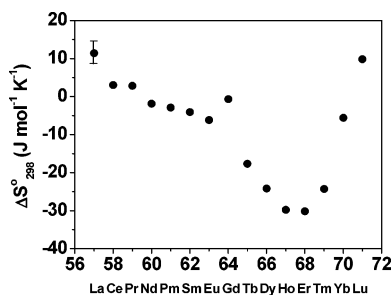
Figure 4. Atomic number dependence of the molar standard entropies for the rare earth element vapor complexes $LnAl_3Br_{12}$ from Ln = La to Ln = Lu reported in this study with the probable overall error ± 3 J mol⁻¹ K⁻¹ (only shown at Ln = La).

measurements, which may lead to the statistical errors not more than ± 0.2 kJ mol⁻¹ for $\Delta G°$ at every temperature, ± 0.7 kJ mol⁻¹ for $\Delta H°_{T_m}$ and ± 1.0 J mol⁻¹ K⁻¹ for $\Delta S°_{T_m}$, where T_m denotes the mean experimental temperatures. These uncertainties, together with that inherent in eq 9 and the error

from the scatter of the experimental points shown in Figures S1−S16, may give rise to the probable overall errors of ±0.5 kJ mol^{-1} for $\Delta G°$, ±1.5 kJ mol^{-1} for $\Delta H°_{T_m}$, and ±2.0 J mol^{-1} K^{-1} for $\Delta S°_{T_m}$ for all LnAl$_3$Br$_{12}$ from Ln = Sc to Ln = Lu. Moreover, the absolute error may be ±1.0 J mol^{-1} K^{-1} for the assumed value of $\Delta C_P° = 0$ J mol^{-1} K^{-1}, which may result in the additional probable uncertainties of not more than ±0.5 kJ mol^{-1} for $\Delta H°_{T_m} - \Delta H°_{298}$ and not more than ±1.0 J mol^{-1} K^{-1} for $\Delta S°_{T_m} - \Delta S°_{298}$. Thus, the probable overall errors may be ±2 kJ mol^{-1} for $\Delta H°_{298}$ and ±3 J mol^{-1} K^{-1} for $\Delta S°_{298}$, respectively, for LnAl$_3$Br$_{12}$ from Ln = Sc to Ln = Lu.

As mentioned above, the literature thermodynamic data of the LnAl$_3$Cl$_{12}$ vapor complexes were mainly determined by using the methods of UV−vis spectrometry,[11,12] radiochemistry,[16,17] and quenching,[18] most of which are in excellent or reasonably good agreement with our previous phase equilibrium-quenching measurements,[21] and only those for LaAl$_3$Cl$_{12}$,[27] NdAl$_3$Cl$_{12}$,[26] and EuAl$_3$Cl$_{12}$[23] were measured by the dynamic method of chemical vapor transport, most of which were published later than ref 21. But the LnAl$_3$-Br$_{12}$ vapor complexes were all determined by the chemical vapor transport method.[25,28] It would be therefore proper to compare our phase equilibrium-quenching measurements with the literature chemical vapor transport data first for the LnAl$_3$Cl$_{12}$ vapor complexes. The thermodynamic properties for the reactions LnCl$_3$(s) + (3/2)Al$_2$Cl$_6$(g) = LnAl$_3$Cl$_{12}$(g) are $\Delta H°_{298} = 47.9$ kJ mol^{-1} and $\Delta S°_{298} = 7.8$ J mol^{-1} K^{-1} for LaAl$_3$Cl$_{12}$, $\Delta H°_{298} = 34.6$ kJ mol^{-1} and $\Delta S°_{298} = -3.3$ J mol^{-1} K^{-1} for NdAl$_3$Cl$_{12}$, and $\Delta H°_{298} = 23.5$ kJ mol^{-1} and $\Delta S°_{298} = -6.3$ J mol^{-1} K^{-1} for EuAl$_3$Cl$_{12}$ and derive from the phase equilibrium-quenching measurements,[21] where the former two have been quoted in refs 26 and 27. These values are in reasonably good agreement with $\Delta H°_{298} = 42$ kJ mol^{-1} and $\Delta S°_{298} = 1$ J mol^{-1} K^{-1} for LaAl$_3$Cl$_{12}$ reported by Oppermann et al.[3,27] and with $\Delta H°_{298} = 26$ kJ mol^{-1} and $\Delta S°_{298} = -11$ J mol^{-1} K^{-1} for EuAl$_3$Cl$_{12}$,[1] which were derived from the thermodynamic data reported by Lange and Bärnighausen,[23] but much smaller than $\Delta H°_{298} = 60$ kJ mol^{-1} and $\Delta S°_{298} = 33$ J mol^{-1} K^{-1} for NdAl$_3$Cl$_{12}$, which were derived from the thermodynamic data reported in ref 26 (or $\Delta H°_{298} = 55$ kJ mol^{-1} as shown in Figure 10 of ref 3). Fortunately, all the $\Delta S°_{298}$ data reported in ref 21 for the LnAl$_3$Cl$_{12}$ vapor complexes from Ln = La to Ln = Lu, including $\Delta S°_{298} = 7.8$ J mol^{-1} K^{-1} for LaAl$_3$Cl$_{12}$, $\Delta S°_{298} = -3.3$ J mol^{-1} K^{-1} for NdAl$_3$Cl$_{12}$, and $\Delta S°_{298} = -6.3$ J mol^{-1} K^{-1} for EuAl$_3$Cl$_{12}$, have recently been used in further thermodynamic calculations in the literature (see, for example, Table 9 in ref 3 and Table 3 in ref 27). Furthermore, Oppermann et al.[3] have recognized the $\Delta H°_{298}$ values from 17 to 46 kJ mol^{-1} and the $\Delta S°_{298}$ values from −17 to 8 J mol^{-1} K^{-1} for all the LnAl$_3$Cl$_{12}$ vapor complexes, which fit almost all the literature data except the above-mentioned values of $\Delta H°_{298} = 60$ (or 55) kJ mol^{-1} and $\Delta S°_{298} = 33$ J mol^{-1} K^{-1} for NdAl$_3$Cl$_{12}$.

The literature thermodynamic data for the LnAl$_3$Br$_{12}$ vapor complexes were determined by Oppermann et al. in terms of the chemical vapor transport method for Ln = Y[3,25] at

about 870−1010 K and for Ln = La[3,28] at about 670−820 K, which are also listed in Table 1. It would seem that the values of $\Delta H°_{298} = 21$ kJ mol^{-1} and $\Delta S°_{298} = -8$ J mol^{-1} K^{-1} for LaAl$_3$Br$_{12}$ reported in ref 3 are somewhat comparable with those of $\Delta H°_{298} = 42.8$ kJ mol^{-1} and $\Delta S°_{298} = 11.4$ J mol^{-1} K^{-1} reported in this study. The molar Gibbs free energies are $\Delta G°_{820} = 28$ kJ mol^{-1} and $\Delta G°_{670} = 22$ kJ mol^{-1} derived from ref 3, while $\Delta G°_{820} = 33.4$ kJ mol^{-1} and $\Delta G°_{670} = 35.2$ kJ mol^{-1} derived from this study. Both show a larger difference at low temperature than at high temperature. On the other hand, from the thermodynamic data reported in ref 25, one may derive the values of $\Delta H°_{298} = 224$ kJ mol^{-1} and $\Delta S°_{298} = 217$ J mol^{-1} K^{-1} for YAl$_3$Br$_{12}$, which are the largest literature values for all the LnAl$_3$X$_{12}$ vapor complexes, not only much larger than those of $\Delta H°_{298} = 37.7$ kJ mol^{-1} and $\Delta S°_{298} = 14.5$ J mol^{-1} K^{-1} for YAl$_3$-Br$_{12}$ reported in this study but also much larger than the second largest literature values for all the LnAl$_3$X$_{12}$ vapor complexes, $\Delta H°_{298} = 60$ (or 55) kJ mol^{-1} and $\Delta S°_{298} = 33$ J mol^{-1} K^{-1} for NdAl$_3$Cl$_{12}$ reported by Oppermann themselves[26] as mentioned above. The molar Gibbs free energies are $\Delta G°_{1010} = 5$ kJ mol^{-1} and $\Delta G°_{870} = 35$ kJ mol^{-1} derived from ref 25, while $\Delta G°_{1010} = 23.1$ kJ mol^{-1} and $\Delta G°_{870} = 25.1$ kJ mol^{-1} derived from this study. Both show a much larger difference at high temperature than at low temperature. Oppermann et al.[28] have discovered the predominant vapor complex to be LaAl$_3$Br$_{12}$ at about 670−820 K but for LaAl$_2$-Br$_9$ to be at about 970−1070 K in the LaBr$_3$−AlBr$_3$ system. Recently, they[3] have also suggested the YAl$_3$Br$_{12}$ to be not the sole vapor complex in the YBr$_3$−AlBr$_3$ system according to their unusually larger molar entropy values for YAl$_3$Br$_{12}$ compared to LaAl$_3$Br$_{12}$. Furthermore, they[3] have recognized the values of $\Delta H°_{298} = 45 \pm 21$ kJ mol^{-1} and $\Delta S°_{298} = -8\pm17$ J mol^{-1} K^{-1} for all the LnAl$_3$Br$_{12}$ vapor complexes, which are much smaller than the above-mentioned values of $\Delta H°_{298} = 224$ kJ mol^{-1} and $\Delta S°_{298} = 217$ J mol^{-1} K^{-1} for YAl$_3$Br$_{12}$. It is known that the dynamic method of chemical vapor transport may be used for thermodynamic measurements only when the transport is steady-state diffusion controlled in the whole process and that the transport conditions may greatly affect the diffusion coefficient and equilibrium constant calculations in some cases.[30] Therefore, the experimental uncertainties in the chemical vapor transport measurements might be the main cause for the difference in the thermodynamic data reported in the literature[3,25,28] and those reported in this study for the LnAl$_3$Br$_{12}$ vapor complexes.

3. Systematics and Anomalies. The standard molar enthalpy and standard molar entropy of the LnAl$_3$Br$_{12}$ vapor complexes from Ln = Sc to Ln = Lu reported in this study allow a systematic analysis of the thermodynamic properties not only against the atomic number of Ln^{3+} from Ln = La to Ln = Lu but also against the ionic radius of Ln^{3+} from Ln = Sc to Ln = Lu.

Figures 3 and 4 show the values of $\Delta H°_{298}$ and $\Delta S°_{298}$ for the LnAl$_3$Br$_{12}$ vapor complexes against the atomic number

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(30) Emmenegger, F. P. *Inorg. Chem.* **1977**, *16*, 343.

of Ln^{3+} from Ln = La to Ln = Lu. It can be seen that the values of the $LnAl_3Br_{12}$ vapor complexes decrease from Ln = La to Ln = Eu and then increase from Ln = Eu to Ln = Gd for ΔH°_{298} and ΔS°_{298} in the left-hand sides and decrease from Ln = Gd to Ln = Ho for ΔH°_{298} but to Ln = Er for ΔS°_{298} and then increase from them to Ln = Lu for ΔH°_{298} and ΔS°_{298} in the right-hand sides. This indicates a significant Gd divergence and two weak minimum points at Ln = Eu and Ho for ΔH°_{298} or at Ln = Eu and Er for ΔS°_{298}, where the difference between $\Delta S^{\circ}_{298} = -29.8$ J mol^{-1} K^{-1} for $HoAl_3Br_{12}$ and $\Delta S^{\circ}_{298} = -30.2$ J mol^{-1} K^{-1} for $ErAl_3Br_{12}$ is within the experimental errors. Here, the Gd divergence is consistent with the half-filled 4f shell and the trends are similar to those of the $LnAl_3Cl_{12}$ vapor complexes.[21] Furthermore, as compared with the $LnAl_3Cl_{12}$ vapor complexes from Ln = La to Ln = Lu, the ΔH°_{298} values of the $LnAl_3Br_{12}$ are smaller from Ln = La to Ln = Ho, are comparable for Ln = Er and Ln = Tm, and are larger for Ln = Yb and Ln = Lu, while the ΔS°_{298} values are larger for Ln = La, are comparable for Ln = Ce, are larger again from Ln = Pr to Ln = Pm, are comparable again for Ln = Sm and Ln = Eu, are smaller from Ln = Gd to Ln = Tm, and are larger again for Ln = Yb and Ln = Lu. They lead to nearly equal ΔH°_{298} and ΔS°_{298} values between $LaAl_3Br_{12}$ and $LuAl_3Br_{12}$ but much larger ΔH°_{298} and ΔS°_{298} values for $LaAl_3Cl_{12}$ than $LuAl_3Cl_{12}$. They also result in a slightly larger ΔH°_{298} value (2.9 kJ mol^{-1}) for $ErAl_3Br_{12}$ than $HoAl_3Br_{12}$ but nearly equal ΔH°_{298} values for $HoAl_3Cl_{12}$ and $ErAl_3Cl_{12}$ (with a difference smaller than the probable overall error ±2 kJ mol^{-1}). These differences indicate again the importance of the halogen anions for the rare earth halide vapor complexes.

It is known that the structure information is essentially important for analyzing the systematics and anomalies in thermodynamic properties of rare earth element compounds and complexes from Ln = Sc to Ln = Lu. However, up to now scientists have different opinions on the microstructures of the rare earth complexes even in the condensed states.[31−34] The gaseous metal halides have recently been appraised as one of the most difficult systems for structure determinations.[35] A large number of experimental and theoretical studies have been reported for the structures of gaseous rare earth halides, which have carefully been discussed in recent reviews,[35,36] and new high-level computations[37,38] have further enhanced our knowledge. The compositions of the rare earth halide vapor complex systems are much more complicated than the gaseous rare earth halide systems. It is

therefore not surprising that there have been only a few studies on the structures of the rare earth halide vapor complexes.

For microstructures of the rare earth halide vapor complexes, Papatheodorou[1,9] has proposed various possible configurations: three for MLnX$_4$; one for LnAX$_6$ (where A = Al, Ga, and In); one for LnA$_2$X$_9$; four for LnA$_3$X$_{12}$; two for LnA$_4$X$_{15}$. In the experimental determinations, Spiridonov et al.[40] have performed an electron diffraction analysis for KYCl$_4$, Metallinou et al.[41] reported the Raman spectra for CsScI$_4$, and Feltrin and Cesaro[42] determined the infrared spectra for MDyCl$_4$ (M = Li, Na, Cs) and LiDyBr$_4$. In the theoretical investigations, Groen et al.[9,10] carried out the quantum chemical calculations for NaLnCl$_4$ (Ln = Ce, Nd), LiLnX$_4$ (Ln = La, Ce, Dy; X = F, Cl, Br, I), and MLaX$_4$ (M = Na, K, Cs; X = F, Cl, Br, I), and Tosi and co-workers[8,9] reported the ionic model calculations for MLnX$_4$ (M = Li, Na; Ln = La, Gd, Lu; X = F, Cl), MLaF$_4$ (M = K, Rb, Cs), KLaCl$_4$, LnACl$_6$ (Ln = La, Nd, Er, Lu; A = Al, Ga), NdGa$_2$Cl$_9$, and NdGa$_3$Cl$_{12}$. Neither experimental determinations nor theoretical calculations are available for the vapor complexes LnAl$_3$Cl$_{12}$ and LnAl$_3$Br$_{12}$ from Ln = Sc to Ln = Lu.[43]

In the three "cluster" type structures suggested by Papatheodorou[1,39] for the LnA$_3$X$_{12}$ (A = Al, Ga, In) vapor complexes, the lanthanide ion preserves the same coordination as in the solid rare earth chlorides reviewed earlier by Brown[44] (e.g., 6-fold for an end lanthanide chloride, 8-fold for a middle lanthanide chloride, and 9-fold for an early lanthanide chloride) and is bound to AX$_4$ by an edge or a face. However, this variation in the coordination number is unlikely to appear in the structures of the rare earth halide solid complexes and gaseous rare earth halides. For example,
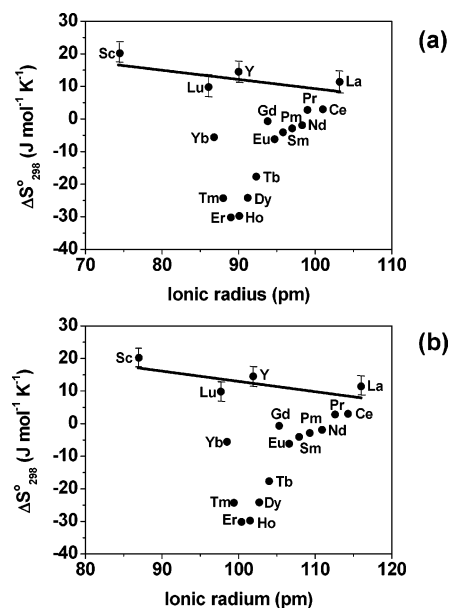
(31) Gschneidner, K. A., Jr. *J. Alloys Compd.* **1993**, *192*, 1.
(32) Gschneidner, K. A., Jr. *J. Alloys Compd.* **1995**, *223*, 165.
(33) Kanno, H. *J. Alloys Compd.* **1993**, *192*, 271.
(34) Karazija, R.; Kyniene, A. *J. Phys. Chem. A* **1998**, *102*, 897.
(35) Hargittai, M. *Chem. Rev.* **2000**, *100*, 2233.
(36) Kovács, A.; Konings, R. J. M. *J. Phys. Chem. Ref. Data* **2004**, *33*, 377.
(37) Saloni, J.; Roszak, S.; Hilpert, K.; Miller, M.; Leszczynski, J. *Eur. J. Inorg. Chem.* **2004**, *1212*.
(38) Saloni, J.; Roszak, S.; Hilpert, K.; Popovic, A.; Miller, M.; Leszczynski, J. *Inorg. Chem.* **2006**, *45*, 4508.

(39) Papatheodorou, G. N. In *Current Topics in Materials Science*; Kaldis, E., Ed.; North Holland Publishing Co.: New York, 1982; Vol. 10, p 249.
(40) Spiridonov, V. P.; Brezgin, Y. A.; Shakhparonov, M. I. *Zh. Strukt. Khim.* **1971**, *12*, 1080.
(41) Metallinou, M. M.; Herstad, O.; Ostvold, T.; Papatheodorou, G. N. *Acta Chem. Scand.* **1990**, *44*, 683.
(42) Feltrin, A.; Cesaro, S. N. *High Temp. Mater. Sci.* **1996**, *35*, 203.
(43) Because no experimental data were available, an estimated value of $\Delta C^{\circ}_P = 0$ J mol^{-1} K^{-1} was first introduced by Schäfer (Schäfer, H. *Angew. Chem.* **1976**, *88*, 775) for the reaction LnCl$_3$(s) + (3/2)Al$_2$Cl$_6$(g) = LnAl$_3$Cl$_{12}$(g) for Ln = Nd and then extended to LnAl$_3$Cl$_{12}$ and LnAl$_3$Br$_{12}$ from Ln = Sc to Ln = Lu as mentioned above. Moreover, the absolute error for $\Delta C^{\circ}_P = 0$ J mol^{-1} K^{-1} was omitted in the literature until we[20−22] introduced an estimated value of ±1.0 J mol^{-1} K^{-1}. Interestingly, to check the value of $\Delta C^{\circ}_P = 0$ J mol^{-1} K^{-1}, one of the reviewers has calculated the molecular structure and the force field for gaseous ScAl$_3$Cl$_{12}$ and Al$_2$Cl$_6$ by ab initio (HF/3-21.G*) and used the results for the calculation of the heat capacity. Although the level of calculation HF/3-21.G* is quite low as pointed out by the reviewer and the value of $C^{\circ}_{P,298}$(Al$_2$Cl$_6$) = 150 J mol^{-1} K^{-1} calculated by the reviewer is obviously different from the literature values, such as $C^{\circ}_{P,298}$(Al$_2$Cl$_6$) = 157.867 J mol^{-1} K^{-1} recommended by Barin,[29] the reviewer advised us to increase the probable overall errors for the standard thermodynamic quantities listed in Table 1. If the absolute error must be increased, for example, to ±2.0 J mol^{-1} K^{-1}, which needs the support of more sophisticated theory, the additional probable uncertainties may give rise to not more than ±0.8 kJ mol^{-1} for $\Delta H^{\circ}_{T_m} - \Delta H^{\circ}_{298}$ and not more than ±1.7 J mol^{-1} K^{-1} for $\Delta H^{\circ}_{T_m} - \Delta S^{\circ}_{298}$, and then the probable overall errors may increase to ±2.3 kJ mol^{-1} for ΔH°_{298} and to ±3.7 J mol^{-1} K^{-1} for ΔS°_{298}, respectively for LnAl$_3$Cl$_{12}$ and LnAl$_3$Br$_{12}$ from Ln = Sc to Ln = Lu.
(44) Brown, D. *Halides of the Lanthanides and Actinides*; Wiley-VCH: New York, 1968.
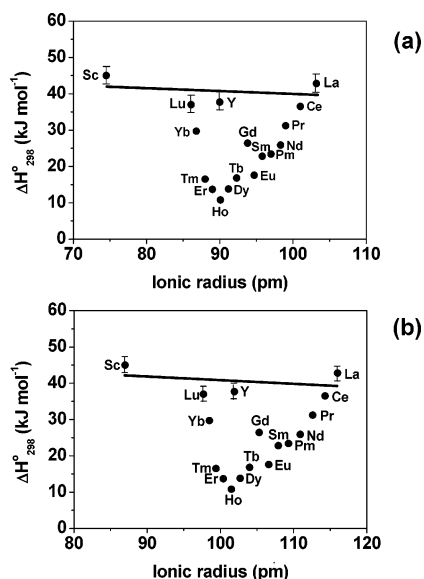
Figure 5. Ionic radius dependence of the molar standard enthalpies for the rare earth element vapor complexes $LnAl_3Br_{12}$ from Ln = Sc to Ln = Lu reported in this study with the probable overall error ± 2 kJ mol^{-1} (only shown at Ln = Sc, Lu, Y, and La): (a) 8-fold coordination; (b) 6-fold coordination.

Figure 6. Ionic radius dependence of the molar standard entropies for the rare earth element vapor complexes $LnAl_3Br_{12}$ from Ln = Sc to Ln = Lu reported in this study with the probable overall error ± 3 J mol^{-1} K^{-1} (only shown at Ln = Sc, Lu, Y, and La): (a) 8-fold coordination; (b) 6-fold coordination.

the experiments suggested the same 8-fold configuration structure for the solid complexes YAl_3Cl_{12},[3,45] $GdAl_3Cl_{12}$,[46] $TbAl_3Cl_{12}$,[46] $DyAl_3Cl_{12}$,[46,47] $HoAl_3Cl_{12}$,[48] $LaAl_3Br_{12}$,[49] $PrAl_3$-Br_{12},[49] and $NdAl_3Br_{12}$[49] and the experimental and theoretical studies[35,36] supported a planar (or quasiplanar) equilibrium structure for gaseous rare earth chlorides, bromides, and iodides. Furthermore, the ionic model calculations[7,8] suggested the structures of the vapor complexes $MLnX_4$ (M = Li, Na; Ln = La, Gd, Lu; X = F, Cl) and $LnACl_6$ (Ln = La, Nd, Er, Lu; A = Al, Ga) to be independent of the rare earth species and the most stable structure for the vapor complex $NdGa_3Cl_{12}$ to be also the 8-fold configuration. Therefore, it would seem proper to assume the same structure for the $LnAl_3Br_{12}$ vapor complexes from Ln = Sc to Ln = Lu. One may then analyze the systematics and anomalies in their thermodynamic properties as functions of the rare earth ionic radius. Figures 5a and 6a show the standard molar enthalpies and standard molar entropies of the $LnAl_3Br_{12}$ vapor complexes from Ln = Sc to Ln = Lu against the rare earth ionic radius with an 8-fold coordination number,[50] which is the same as the vapor complex $NdGa_3Cl_{12}$ and the solid complexes $LnAl_3Cl_{12}$ (where Ln = Y, Gd, Tb, Dy, and Ho) and $LnAl_3Br_{12}$ (where Ln = La, Pr, and Nd) as mentioned above. It can be seen that the four vapor complexes $ScAl_3Br_{12}$, $LuAl_3Br_{12}$, YAl_3Br_{12}, and $LaAl_3Br_{12}$ have the largest ΔH°_{298} and ΔS°_{298} values and nearly lie on straight lines. (The experimental deviations from the linearity are almost within the probable overall errors, ± 2.0 kJ mol^{-1} for ΔH°_{298} and ± 3.0 J mol^{-1} K^{-1} for ΔS°_{298}). However, the

properties of the $LnAl_3Br_{12}$ complexes of middle and light lanthanides from Ln = Yb to Ln = Ce are anomalous. To obtain a deeper insight into the systematics and anomalies, Figures 5b and 6b show the ΔH°_{298} and ΔS°_{298} against rare earth ionic radius with a 6-fold coordination number[50] from Ln = Sc to Ln = Lu. The close similarity between Figure 5a,b and between Figure 6a,b suggests that the systematics and anomalies in the $LnAl_3Br_{12}$ vapor complexes are independent from the coordination number assumptions.

It is know that Sc^{3+} and Y^{3+} have no 4f electrons, Lu^{3+} has no unpaired 4f electrons, and normally La^{3+} also has no 4f electrons. Therefore, the linear or nearly linear manner of the standard molar enthalpies and standard molar entropies vs rare earth ionic radius for the vapor complexes $ScAl_3$-Br_{12}, $LuAl_3Br_{12}$, YAl_3Br_{12}, and $LaAl_3Br_{12}$ might be related to no unpaired 4f electrons in the four rare earth element ions. If this argument is also true for the rare earth chloride vapor complexes, the unknown ΔH°_{298} and ΔS°_{298} values of $ScAl_3Cl_{12}$ and YAl_3Cl_{12} might be estimated from the known values of $LaAl_3Cl_{12}$ and $LuAl_3Cl_{12}$ reported in ref 21 in terms of the linear dependence of ΔH°_{298} and ΔS°_{298} on rare earth ionic radius. The results are $\Delta H^\circ_{298} = 12.3$ kJ mol^{-1} and $\Delta S^\circ_{298} = -17.7$ J mol^{-1} K^{-1} for $ScAl_3Cl_{12}$ and $\Delta H^\circ_{298} = 31.6$ kJ mol^{-1} and $\Delta S^\circ_{298} = -3.9$ J mol^{-1} K^{-1} for YAl_3Cl_{12}, which may yield $\Delta G^\circ_{600} = 22.9$ kJ mol^{-1} and $\Delta G^\circ_{800} = 26.5$ kJ mol^{-1} for $ScAl_3Cl_{12}$ and $\Delta G^\circ_{600} = 33.9$ kJ mol^{-1} and $\Delta G^\circ_{800} = 34.7$ kJ mol^{-1} for YAl_3Cl_{12}. On the other hand, the values of standard enthalpies and standard entropies reported in ref 17 may yield $\Delta G^\circ_{600} = 13.9$ kJ mol^{-1} and $\Delta G^\circ_{800} = 15.3$ kJ mol^{-1} for $ScAl_2Cl_9$ and $\Delta G^\circ_{600} = 23.0$ kJ mol^{-1} and $\Delta G^\circ_{800} = 23.9$ kJ mol^{-1} for YAl_2Cl_9. These data clearly indicate that the $ScAl_2Cl_9$ and YAl_2Cl_9 vapor complexes are much more stable than the $ScAl_3Cl_{12}$ and YAl_3Cl_{12} vapor complexes at the experimental temperatures. This is consis-

(45) Hennig, Z.; Oppermann, H.; Ehrlich, S.; Mattausch, M.; Simon, A. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1414.
(46) Shamir, J.; Hake, D.; Urland, W. *J. Raman Spectrosc.* **1992**, *23*, 137.
(47) Hake, D.; Urland, W. *Z. Anorg. Allg. Chem.* **1990**, *586*, 99.
(48) Hake, D.; Urland, W. *Angew. Chem.* **1989**, *101*, 1416.
(49) Hake, D.; Urland, W. *Z. Anorg. Allg. Chem.* **1992**, *613*, 45.
(50) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

tent with our previous measurements,[19] where only the $ScAl_2Cl_9$ and YAl_2Cl_9 vapor complexes were detected.

Although outside the scope of this paper, we noted that when searching the systematics and anomalies in physical and chemical properties of pure metals, compounds, and alloys in the solid state and EDTA complexes in aqueous solutions, Gschneidner[32,33] has discovered their linear or nearly linear dependence on the metallic or ionic radius of the three rare earth elements Sc, Y, and Lu and their higher property values than all the other rare earth elements. Moreover, he assumed 4f electron hybridization for La and argued the lower values for the solid and liquid systems from Ln = La to Ln = Yb to be all caused by the unpaired 4f electrons. Furthermore, he assumed a pseudo-La without unpaired 4f electrons and extended the linear trends from the three elements Sc, Lu, and Y to the pseudo-La. Here, the Sc, Lu, Y, and pseudo-La in the solid and liquid systems having no unpaired 4f electrons and having linear trends in their properties against the rare earth atomic or ionic radius are similar to the Sc, Lu, Y, and La in the $LnAl_3X_{12}$ vapor complexes reported in this study. Therefore, further experimental and theoretical studies on the microstructures of the vapor complexes $LnAl_nBr_{3n+3}$ and $LnAl_nCl_{3n+3}$ from Ln = Sc to Ln = Lu will be very interesting and will provide a deeper understanding of the systematics and anomalies in their thermodynamic properties.

Conclusions

This paper presents a systematic study on the complexation reactions $LnBr_3(s) + (n/2)Al_2Br_6(g) = LnAl_nBr_{3n+3}(g)$ in the $LnBr_3-AlBr_3$ binary systems by the phase equilibrium-quenching measurements in the temperature range $601-833$ K and pressure range $0.01-0.22$ MPa for the 16 rare earth elements Ln = Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu and by interpolation for the radioelement Ln = Pm. The results show that the $LnAl_3Br_{12}$ complexes are the sole stable vapor complexes for all the rare earth elements under the same reaction conditions. In total for all the 17 vapor complexes $LnAl_3Br_{12}$, the four complexes $ScAl_3Br_{12}$, $LuAl_3Br_{12}$, YAl_3Br_{12}, and $LaAl_3Br_{12}$ without unpaired 4f electrons have higher standard enthalpies and standard entropies than the complexes of the other 13 rare earth elements with unpaired 4f electrons. Moreover, the property values of the four vapor complexes show nearly linear dependence on their rare earth ionic radius. Furthermore, the standard enthalpies and standard entropies of the vapor complexes $LnAl_3Br_{12}$ from Ln = La to Ln = Lu against the rare earth atomic number show significant Gd divergence.

Supporting Information Available: Experimental quenching data for the vapor complexes $LnAl_nBr_{3n+3}$ of the 16 rare earth elements Ln = Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu (Tables S1–S16) and plots of $\ln(p_{LnAl_nBr_{3n+3}}/p°)$ vs $\ln(p_{Al_2Br_6}/p°)$ of the same 16 rare earth elements (Figure S1). The material is available free of charge via the Internet at http://pubs.acs.org.

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