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Vapor species over cerium and samarium trichlorides, enthalpies of formation of $(LnCl_3)_n$ molecules and $Cl^-(LnCl_3)_n$ ions

A. M. Pogrebnoi[1], L. S. Kudin[1]*, V. B. Motalov[1] and V. F. Goryushkin[2]

[1]State University of Chemical Sciences and Technology, Prospect Engelsa 7, Ivanovo 153460, Russia
[2]Siberian State Industrial University, ul. Kirova 42, Novokuznetsk 654007, Russia

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A Knudsen effusion cell mass spectrometric technique was used to study vapor species over $CeCl_3$ and $SmCl_3$. Monomer, dimer, and trimer (Sm_3Cl_9) molecules, and $LnCl_4^-$, $Ln_2Cl_7^-$, $Ln_3Cl_{10}^-$ (Ln = Ce, Sm) negative ions, were observed in saturated vapor in the temperature range 958–1227 K. Partial vapor pressures of neutral constituents were determined and the enthalpies of sublimation ($\Delta_s H$, 298 K, kJ·mol^{-1}) to monomers and associated molecules obtained: 328 ± 6 ($CeCl_3$), 306 ± 6 ($SmCl_3$), 453 ± 16 (Ce_2Cl_6), 408 ± 12 (Sm_2Cl_6), and 468 ± 40 (Sm_3Cl_9). Equilibrium constants for various chemical reactions were measured and the enthalpies of reactions obtained using the second and third laws of thermodynamics. The enthalpies of formation ($\Delta_f H$, 298 K, kJ·mol^{-1}) of molecules and ions have been calculated as follows: -730 ± 6 ($CeCl_3$), -722 ± 6 ($SmCl_3$), -1663 ± 16 (Ce_2Cl_6), -1649 ± 13 (Sm_2Cl_6), -2617 ± 40 (Sm_3Cl_9), -1250 ± 15 ($CeCl_4^-$), -1252 ± 15 ($SmCl_4^-$), -2184 ± 35 $Ce_2Cl_7^-$), -2172 ± 26 ($Sm_2Cl_7^-$), -3183 ± 43 ($Ce_3Cl_{10}^-$), and -3147 ± 43 ($Sm_3Cl_{10}^-$). Copyright © 2001 John Wiley & Sons, Ltd.

Lanthanide halides are considered to be attractive compounds for experimental and theoretical investigations due to their importance for various technological applications related to the fabrication of new materials with controlled properties. Another important role of lanthanide halides appears in the design of protection systems for cases of nuclear reactor accidents.[1] Thus, data on lanthanide halides are urgently needed.

Thermodynamic properties are known to be dependent on individual constituents of vapor. It has been shown recently[2–8] that the composition of saturated vapor over lanthanide trichlorides is complicated. Along with monomers, molecular and ionic clusters occur. Extremely high degrees of association have been observed for lutetium[3] and thulium[8] trichlorides. In particular, species as large as $(LuCl_3)_6$, $(TmCl_3)_5$, $Lu_6Cl_{19}^-$, and $Tm_8Cl_{25}^-$ have been discovered in our previous investigations. Hence, association in the vapor phase is likely to be a distinctive property of lanthanide trichlorides.

The purpose of the present study was to establish the composition of saturated vapor over cerium and samarium trichlorides, and to obtain data on the thermochemical properties of molecules and ions.

*Correspondence to: L. S. Kudin, State University of Chemical Sciences and Technology, Prospect Engelsa 7, Ivanovo 153460, Russia.
E-mail: kudin@isuct.ru

EXPERIMENTAL

A magnetic sector mass spectrometer MI 1201 (90°, 200 mm), modified for high-temperature studies, was used. The ion source permitted work in two regimes. The first allowed conventional electron impact ionization (EI) of molecular beams effusing from the Knudsen cell to be analyzed. In the second regime, the charged vapor species were analyzed. In this case the ions produced via self-surface thermal ionization (TI) inside the effusion cell were drawn out from the cell by a weak electric field. The details of the experimental arrangements are given elsewhere.[2–5]

Reagent-grade cerium or samarium trichloride was loaded into the molybdenum effusion cell under atmospheric pressure from the sealed capsules. The ratio of the evaporation surface area of the cell to the orifice area was about 400. To bake out moisture absorbed, the samples were dried inside the cell at a temperature of about 150°C in a low vacuum of $10–10^{-1}$ Pa for 5–10 h.

The preparation of the substances was carried out using chlorination of the oxides. The chlorinating agent was CCl_4 (commercial, high purity). The oxides CeO_2 and Sm_2O_3, both 99.99 mass-per-cent purity, were received from Verkhnyaya Pyshma, Russia (P.O. Box M-5649). The preparation procedure is described in detail elsewhere.[9] The results of chemical analysis of the cerium and samarium trichlorides thus obtained are shown in Table 1. The solubility of the salts in water was absolute (no insoluble residue).

The substances were placed in Pyrex capsules that were then evacuated and flame-sealed.

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Table 1. Analysis of cerium and samarium trichloride samples; w represents mass-per-cent fractions[a]

LnCl$_3$	Ln[b]		Cl[c]		Σw	$n(Cl)/n(Ln)$
	obs.	calc.	obs.	calc.		
CeCl$_3$	56.63 ± 0.22	56.85	42.88 ± 0.05	43.15	99.51 ± 0.22	2.992 ± 0.010
SmCl$_3$	58.51 ± 0.06	58.57	41.39 ± 0.10	41.43	99.90 ± 0.12	2.999 ± 0.022

[a] Uncertainties are the statistical errors corresponding to 95% confidence interval.
[b] Complexometric titration with EDTA disodium salt.
[c] Gravimetry, in the form of AgCl.

Table 2. Electron impact ionization mass spectra

LnCl$_3$	T (K)	E (eV)	Relative ion intensities					
			Ln$^+$	LnCl$^+$	LnCl$_2^+$	LnCl$_3^+$	Ln$_2$Cl$_5^+$	Ln$_3$Cl$_8^+$
CeCl$_3$	1063	50	12.1	10.6	100	5.0	0.39	
	1197[a]	50	11.6	10.3	100	6.1	0.91	
SmCl$_3$	989	75	22.5	9.0	100	8.6	2.17	
	1109[b]	75	20.0	8.0	100	7.3	4.72	0.01

[a] Doubly charged ions Ce^{++}, CeCl^{++}, and CeCl$_2^{++}$ were also detected.
[b] Doubly charged ions Sm^{++} and SmCl^{++} were also detected. In addition, the ions Sm$_2$Cl$_4^+$ (0.08) were observed (the relative ion intensity is given in parentheses).

RESULTS AND DISCUSSION

Neutral vapor constituents

Mass spectra
Relative ion intensities registered in the EI mass spectra, corrected for isotopic distributions, are listed in Table 2. Mass spectra obtained in this work correspond closely to those reported in the literature.[10–12] Identification of ions was performed by measuring mass-to-charge ratios and through comparison of relative ion abundances with those found by calculation of isotopic abundances. In contrast to mass spectra available in the literature,[10–12] doubly charged ions and ions formed from trimer molecules (Sm$_3$Cl$_9$) were observed.

A separate run, carried out with a fast temperature rise of the samarium trichloride sample up to $T = 1203$ K, resulted in the following mass spectrum: Sm$^+$ (25.3), SmCl$^+$ (13.9), SmCl$_2^+$ (100), SmCl$_3^+$ (4.8), Sm$_2$Cl$_5^+$ (0.14), Sm$_2$Cl$_4^+$ (0.1), Sm^{++} (20.2), and SmCl^{++} (5.5). Increase of Sm$^+$, SmCl$^+$ and decrease of SmCl$_3^+$ relative ion current intensities, compared with those listed in Table 2 for lower temperatures, emphasize that samarium trichloride undergoes dissociation. The observed decrease of the relative abundance of Sm$_2$Cl$_5^+$ confirms this conclusion.

The appearance of Sm$_2$Cl$_4^+$ ions in the mass spectrum cannot be explained either by the ionization of Sm$_2$Cl$_4$ or by that of Sm$_2$Cl$_6$ dimers. First, Sm$_2$Cl$_4$ molecules were not found in the earlier investigation of SmCl$_2$.[13] Second, a contribution of more extensive fragmentation of the dimers Sm$_2$Cl$_6$, in this case, should be negligible (as indicated by a comparison of the 1203 K mass spectrum given above and that in Table 2 for 1109 K). Therefore, we suggest that the main precursors of Sm$_2$Cl$_4^+$ ions are likely to be associated SmCl$_2 \times$ SmCl$_3$ molecules. It is of interest that the existence of the intermolecular compound 2SmCl$_2 \times$ SmCl$_3$ was proved by Goryushkin.[14] Consequently, to some extent, the

fast heating of the sample (see above) makes for a partial reduction of the samarium trichloride to the dichloride.

We suppose that residual moisture in the sample, not completely removed during the fast heating, led to a partial reduction of the trichloride. Such behavior is similar to that of ytterbium trichloride[5] and, in this case, the observed mass spectrum is appropriate for a binary system SmCl$_2$–SmCl$_3$.

The assignment of the ions to their neutral precursors was made taking into account the following items: (i) the shapes of the ionization efficiency curves (IECs), (ii) the appearance energies (*AE*) of ions, and (iii) the temperature dependences of the ion current intensities (*I*), ln(*IT*) = *f*(1/*T*).

The shapes of the IECs shown in Figs 1 and 2 do not exhibit
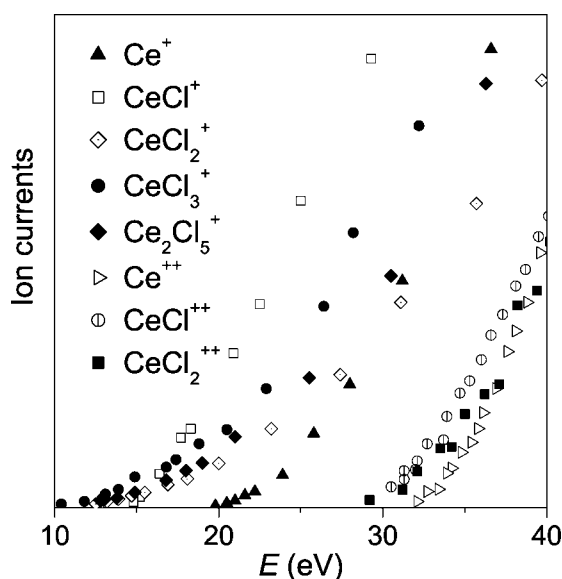
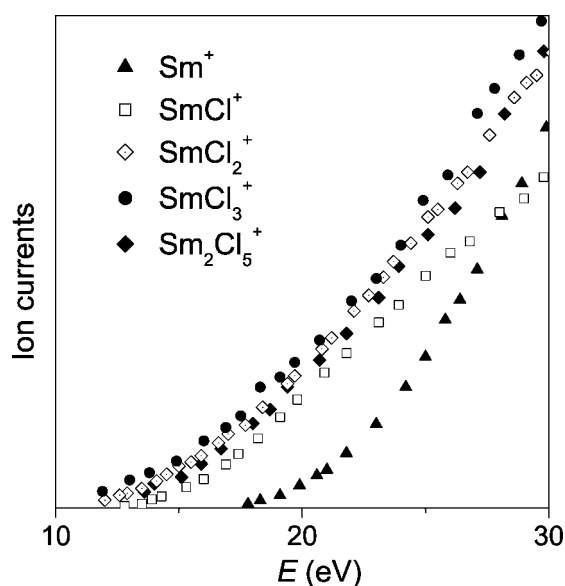**Figure 1.** Ionization efficiency curves for CeCl$_3$, T = 1075 K (1115 K for Ce$_2$Cl$_5^+$).

Figure 2. Ionization efficiency curves for SmCl$_3$, $T = 989$ K.

Figure 3. Temperature dependences of the ion current intensities for CeCl$_3$:

$\ln[I(Ce^+)T] = (-35.35 \pm 0.48) \times (10^3/T) + (47.85 \pm 0.47);$
$\ln[I(CeCl^+)T] = (-35.14 \pm 0.47) \times (10^3/T) + (47.51 \pm 0.46);$
$\ln[I(CeCl_2^+)T] = (-36.67 \pm 0.51) \times (10^3/T) + (51.12 \pm 0.50);$
$\ln[I(CeCl_3^+)T] = (-36.47 \pm 0.99) \times (10^3/T) + (47.76 \pm 0.97);$
$\ln[I(Ce_2Cl_5^+)T] = (-50.17 \pm 1.14) \times (10^3/T) + (58.28 \pm 1.10).$

Uncertainties following the $\pm$ sign include the statistical errors corresponding to 95% confidence interval.

any evident breaks. The ion appearance energies, determined by a linear extrapolation method applied to the corresponding IECs, are given in Table 3. The values obtained in this work are not in conflict with more accurate data of Evdokimov *et al.*[12,15] The *AE* values for doubly charged and Ln$_2$Cl$_5^+$ ions have been determined here for the first time.

The temperature dependences (Figs 3–6) of the ion current intensities were studied for Ln$^+$, LnCl$^+$, LnCl$_2^+$, LnCl$_3^+$ and Ln$_2$Cl$_5^+$ ions. Two runs were carried out for SmCl$_3$; in the second run, only SmCl$_2^+$ and Sm$_2$Cl$_5^+$ ion currents were monitored. As can be seen in Fig. 3, the slopes for Ce$^+$, CeCl$^+$, CeCl$_2^+$, and CeCl$_3^+$ are close to one another and are apparently lower than for Ce$_2$Cl$_5^+$. In the case of SmCl$_3$, the slope for SmCl$_3^+$ appeared to be slightly lower than those for Sm$^+$, SmCl$^+$, and SmCl$_2^+$ ions. Nevertheless, we are inclined to consider all of these slopes as similar, taking into account the rather high dispersion of the measurements due to relatively low intensities of SmCl$_3^+$ ion currents. At the same time, the slope of the temperature dependence of the intensity of Sm$_2$Cl$_5^+$ ions, as shown in Figs 4 and 5, is clearly higher than those for Sm$^+$, SmCl$^+$, and SmCl$_2^+$ ions.

Analysis of the data allowed us to conclude that ions Ln$^+$, LnCl$^+$, LnCl$_2^+$, and LnCl$_3^+$ are formed through ionization and fragmentation of LnCl$_3$ molecules. On the other hand, the ions Ln$_2$Cl$_5^+$ and Sm$_3$Cl$_8^+$ result from the dissociative ionization of dimers Ln$_2$Cl$_6$ and trimers Sm$_3$Cl$_9$, respectively.
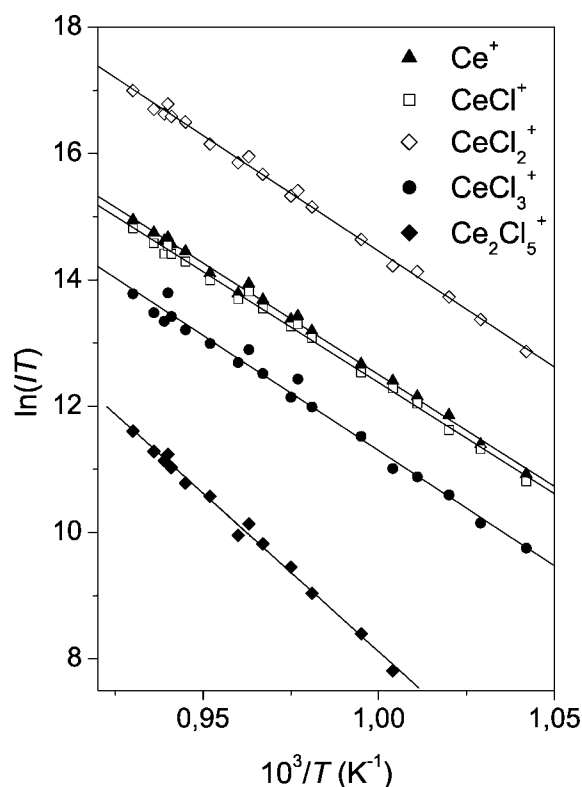
Partial pressures

The partial vapor pressures of neutral constituents have been determined by the conventional mass spectrometric method using the following relationship:

$$p = \frac{KT}{\sigma} \sum_i \frac{I_i}{\gamma_i a_i} \tag{1}$$

where p is the partial pressure of the neutral species; K is the instrumental sensitivity constant; T is the temperature of the cell; σ is the total ionization cross-section at the operating electron energy; ΣI_i is the total ion current of all types of ions formed from the species considered; γ is the gain of the

Table 3. Appearance energies, *AE* (eV)[a], **of ions**

LnCl$_3$	LnCl$_3^+$	LnCl$_2^+$	LnCl$^+$	Ln$^+$	Ln$_2$Cl$_5^+$	Ref.
CeCl$_3$	10.6 ± 0.5	12.4 ± 0.5	15.8 ± 0.5	21.4 ± 0.5	14.3 ± 0.5	This work
	10.22 ± 0.07	12.3 ± 0.05	15.92 ± 0.07	21.17 ± 0.06		13
SmCl$_3$	11.0 ± 0.5	13.2 ± 0.5	15.1 ± 0.5	20.8 ± 0.5	13.5 ± 0.5	This work
	9.75 ± 0.05	14.12 ± 0.06	15.41 ± 0.05	20.10 ± 0.05		16

[a] The energy scale of ionizing electrons was calibrated with respect to Hg.
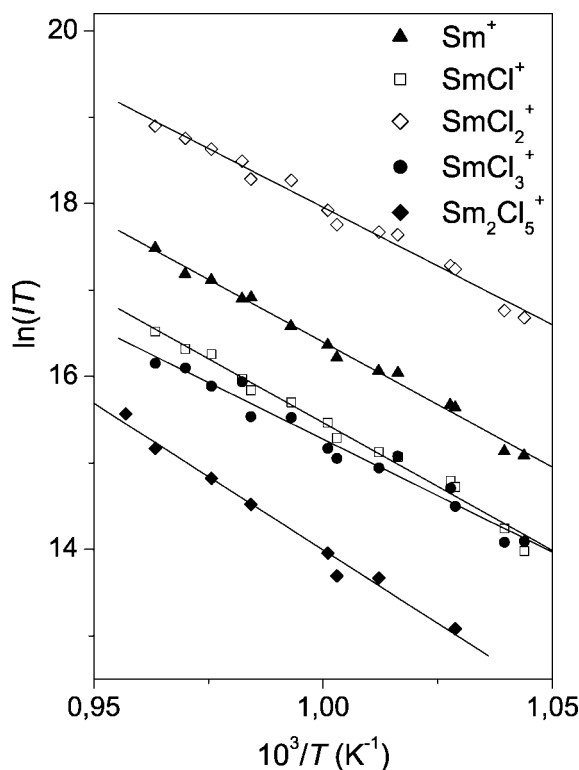 $AE(Ce^{++}) = 31.7 \pm 0.7$ eV; $AE(CeCl^{++}) = 29.8 \pm 0.7$ eV; $AE(CeCl_2^{++}) = 28.6 \pm 0.7$ eV.

Figure 4. Temperature dependences of the ion current intensities for $SmCl_3$ (1st run):

$\ln[I(Sm^+)T] = (-28.94 \pm 0.77) \times (10^3/T) + (45.34 \pm 0.77);$
$\ln[I(SmCl^+)T] = (-29.59 \pm 1.00) \times (10^3/T) + (45.06 \pm 1.00);$
$\ln[I(SmCl_2^+)T] = (-27.19 \pm 0.95) \times (10^3/T) + (45.15 \pm 0.96);$
$\ln[I(SmCl_3^+)T] = (-26.16 \pm 1.41) \times (10^3/T) + (41.43 \pm 1.41);$
$\ln[I(Sm_2Cl_5^+)T] = (-33.95 \pm 1.63) \times (10^3/T) + (47.95 \pm 1.61).$

Figure 5. Temperature dependences of the ion current intensities for $SmCl_3$ (2nd run):

$\ln[I(SmCl_2^+)T] = (-27.50 \pm 0.57) \times (10^3/T) + (44.07 \pm 0.56);$
$\ln[I(Sm_2Cl_5^+)T] = (-31.86 \pm 1.16) \times (10^3/T) + (44.84 \pm 1.11).$

The temperature dependences of vapor pressures were fitted by a least-squares treatment to the following equation:

$$\ln p(\text{atm}) = -A \times \frac{10^3}{T} + B \qquad (2)$$

The values of the A and B coefficients are given in Table 5.

The temperature dependences of partial vapor pressures obtained in this work are shown in Figs 6 and 7 together with the reference data. Our results for monomers and dimers compare well with data obtained at higher temperatures for $CeCl_3$ and estimated for $SmCl_3$ by Polyachenok.[17] The data for $CeCl_3$ monomers, as shown in Fig. 6, agree well with the data of Shimazaki and Niwa,[18] and are not in conflict with

secondary electron multiplier (we assumed $\gamma \sim M^{-1/2}$ where M is the molecular mass of the ion); and a is the natural abundance of the corresponding isotope. The value of K was determined in a separate calibration experiment with silver as reference substance. The ionization cross-sections of molecules have been evaluated by an additivity rule taking into account an empirical correction according to the expression:[16] $\sigma = 0.75\Sigma\sigma_I$, where σ_i is the atomic cross-section taken from Ref. 16. The partial vapor pressures of neutral constituents found in this work are summarized in Table 4.
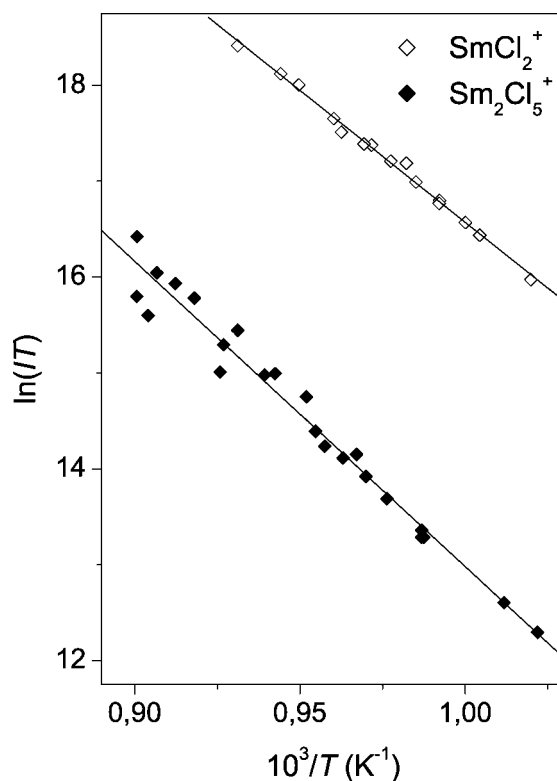
Table 4. Experimental partial pressures of molecules

| $LnCl_3$	$-\ln p$ (atm), T (K)
$CeCl_3$	13.46, 1041; 12.82, 1059; 12.69, 1065; 12.32, 1075; 12.60, 1068; 12.73, 1062; 13.16, 1050; 13.63, 1035; 13.97, 1025; 14.15, 1019; 14.66, 1005; 15.05, 996; 15.56, 980; 15.93, 972; 16.43, 959; 15.17, 990; 13.89, 1024; 13.35, 1039; 12.54, 1063
Ce_2Cl_6	22.19, 1041; 21.37, 1059; 21.01, 1065; 20.54, 1075; 20.87, 1068; 21.12, 1062; 21.58, 1050; 22.33, 1035; 22.70, 1025; 23.11, 1019; 23.75, 1005; 24.34, 996; 22.01, 1039; 20.91, 1063
$SmCl_3$	1st run: 12.27, 973; 11.91, 984; 11.30, 1007; 11.06, 1018; 10.79, 1031; 10.63, 1038; 10.91, 1025; 11.24, 1016; 11.63, 999; 11.89, 988; 12.32, 972; 12.88, 958; 12.80, 962; 11.79, 997
	2nd run: 10.94, 1018; 10.75, 1029; 10.62, 1039; 9.71, 1074; 10.01, 1059; 10.12, 1053; 10.47, 1041; 10.74, 1032; 10.92, 1023; 11.14, 1015; 11.33, 1008; 11.36, 1008; 11.56, 1000; 11.69, 996; 12.15, 980
Sm_2Cl_6	1st run: 14.57, 1045; 14.97, 1038; 15.32, 1025; 15.62, 1016; 16.19, 999; 16.48, 988; 17.06, 972; 16.45, 997
	2nd run: 15.99, 1034; 15.39, 1051; 15.15, 1061; 14.70, 1074; 14.36, 1089; 13.72, 1110; 14.10, 1103; 14.21, 1096; 14.85, 1079; 15.16, 1065; 15.75, 1047; 16.22, 1031; 16.03, 1038; 16.46, 1024; 16.86, 1013; 16.78, 1013; 17.54, 988; 17.85, 979; 16.86, 1013; 15.91, 1044; 15.13, 1080; 14.34, 1110; 14.54, 1106
Sm_3Cl_9	2nd run: 19.87, 1093; 19.16, 1109; 19.70, 1107; 20.78, 1068
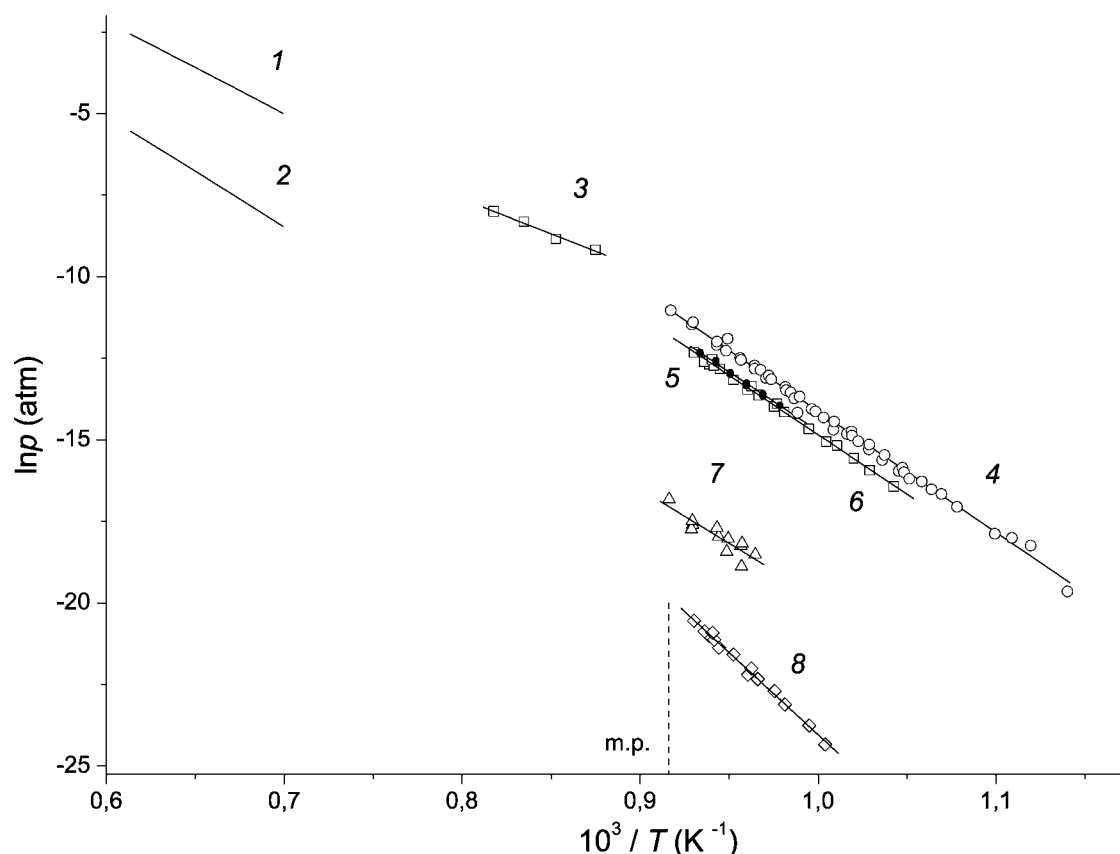
Figure 6. Temperature dependences of vapor pressure over cerium trichloride: *1*-monomer;[17] *2*-dimer;[17] *3*-total pressure;[19] *4*-monomer;[10] *5*-total pressure;[18] *6*-monomer, this work; *7*-dimer;[10] *8*-dimer, this work.

the results reported by Moriarty[19] and Miller and co-workers.[10] As regards the monomer, $SmCl_3$, and dimer, Ce_2Cl_6, the partial pressures obtained by us are approximately one order of magnitude lower than those from Refs 20 and 10, respectively.

Enthalpies of sublimation

The data on the temperature dependences obtained in this work have been used to calculate the sublimation enthalpies and entropies on the basis of the second and third laws of thermodynamics. The results of the calculations are given in Table 6. The thermodynamic functions of the molecules were calculated by the method of statistical thermodynamics in the rigid rotator-harmonic oscillator approximation, with the use of the reference data for $CeCl_3$[21] and $SmCl_3$[22] and the data on molecular constants estimated by us for other molecules (Table 7). The estimation approach is described briefly in the footnotes to Table 7. Thermodynamic functions at selected temperatures are given in Table 8. The Gibbs energy functions, $\Phi^\circ(T) = -(G_T^\circ - H_0^\circ)/T$, for a wide temperature range (from 298.15–2000 K), were approximated as in Ref. 16 by the following equation:

$$\Phi^\circ(T) = a + b\ln x + cx^2 + dx^{-1} + ex + fx^2 + gx^3$$
$$(\text{J} \cdot \text{K}^{-1}\,\text{mol}^{-1};\; x = T \cdot 10^{-4}). \tag{3}$$

The coefficients for Eqn. (3) are collected in Table 9.

The thermodynamic functions of $LnCl_3$ were computed

for the pyramidal (C_{3v}) and planar (D_{3h}) symmetries on the basis of molecular constants taken from Refs 22 and 21, respectively. The difference in the Gibbs energy functions for the two structures is 5.8 J·mol^{-1}·K^{-1} (1000 K).

Here we note that the best agreement between the second and third law values obtained for the sublimation enthalpies was achieved when the planar structure was adopted for $CeCl_3$ according to Myers and Graves,[21] and the pyramidal structure for $SmCl_3$ molecules according to Zasorin.[22] The thermodynamic functions for $CeCl_3$ and $SmCl_3$ in the condensed phase, required for the calculations, were taken from the IVTANTHERMO-96 database[26] and are given at selected temperatures in Table 8.

The enthalpies of sublimation evaluated from the two independent methods, listed in Table 6, are in good agreement with each other and agree, to within experimental

Table 5. Values of *A* and *B* coefficients in Eqn ((2))

Molecule	Temperature range (K)	*A*	*B*
$CeCl_3$	959–1075	35.61 ± 0.72	21.97 ± 1.44
Ce_2Cl_6	996–1075	49.95 ± 1.92	26.06 ± 1.80
$SmCl_3$	980–1074	27.31 ± 0.72	15.73 ± 1.44
Sm_2Cl_6	979–1110	31.06 ± 1.44	13.02 ± 1.80

The overall uncertainties following the ± sign include the statistical errors corresponding to 95% confidence interval and also the systematic errors in the sensitivity constant, ionization cross-sections, and temperature.
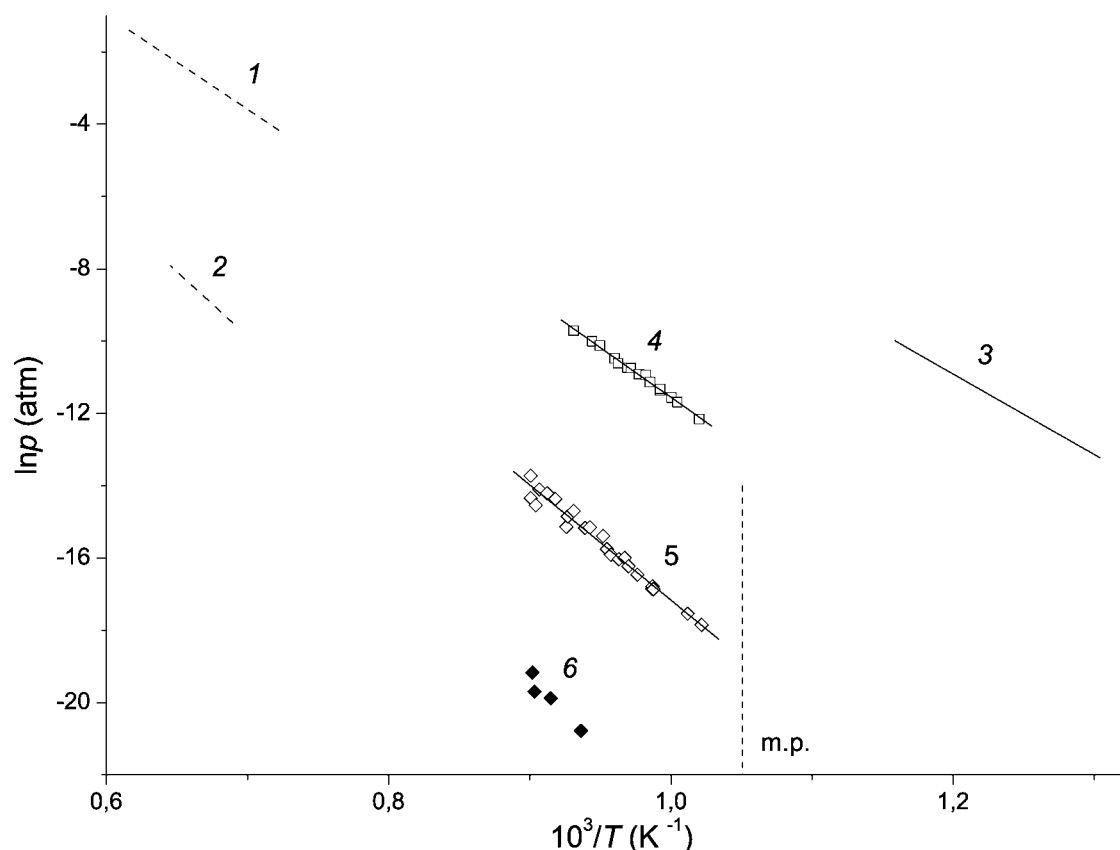
Figure 7. Temperature dependences of vapor pressure over samarium trichloride: *1*-estimation for monomer;[17] *2*-estimation for dimer;[17] *3*-total pressure;[20] *4*-monomer, this work; *5*-dimer, this work; *6*-trimer, this work.

uncertainties, with the reference data with the exception of the values calculated from the data taken from Ref. 20. Experimental values of sublimation enthalpies to Sm_2Cl_6 and Sm_3Cl_9 molecules have been determined in this work for the first time.

The agreement between the enthalpies for sublimation of cerium trichloride to Ce_2Cl_6 molecules obtained in this work and those found by Miller *et al.*[10] seems to be ambiguous at first sight, since the partial pressures found for dimers Ce_2Cl_6 differ distinctly, as mentioned above. It is obvious that the higher the partial pressure, the less is the value of the sublimation enthalpy. Hence, there should be a cancellation of the discrepancy.

Miller and co-workers[10] found molecular constants as a result of theoretical calculations (given in Table 7 together with our estimates). The interatomic distances given by these authors,[10] listed in Table 7, are in agreement with our estimates. However, the frequencies reported in their work are somewhat lower then ours.

As one can judge from the literature,[28] theoretical computations, even for the simplest $LnCl_3$ molecules, yield as a rule lower frequencies in comparison with experimental values. Thus we suggest that this might be the case for the dimers Ce_2Cl_6 reported by Miller and co-workers.[10] The Gibbs energy functions based on the set of molecular constants from that work are, at 1000 K, higher by approximately 30 $J \cdot mol^{-1} \cdot K^{-1}$ than those obtained on the basis of our set. In this way this difference compensates for the higher partial pressure of Ce_2Cl_6 reported by Miller *et*

al.[10] and results in a fortuitous agreement between the data. Nevertheless, our data on the partial pressures of the dimers are consistent with a trend observed in going from $LaCl_3$ to the heavier lanthanide trichlorides,[2,3,5–8] and on this basis may be considered to be reliable.

The enthalpies of formation of molecules summarized in Table 10 were determined by a combination of the sublimation enthalpies with the formation enthalpies of the substances in the condensed phase,[27] $\Delta_f H°$(298 K), -1058.1 ± 0.7 ($CeCl_3$) and -1028.4 ± 2.5 $kJ \cdot mol^{-1}$ ($SmCl_3$). Our values -730 ± 6 ($CeCl_3$), -722 ± 6 $kJ \cdot mol^{-1}$ ($SmCl_3$) agree, within the uncertainties, with the values -729 ± 6, and -707 ± 6 $kJ \cdot mol^{-1}$, respectively, determined by Evdokimov *et al.*,[12] and with -724 ± 21 ($CeCl_3$), -715 ± 26 $kJ \cdot mol^{-1}$ ($SmCl_3$) reported by Polyachenok.[17] It should be noted that the values reported by Evdokimov *et al.*[12] were obtained by procedures which were not connected with absolute vapor pressure measurements but were based on the appearance energy, $AE(Ln^+/LnCl_3)$. However, the values -677 ± 30 $kJ \cdot mol^{-1}$ ($CeCl_3$) and -835 ± 30 ($SmCl_3$), derived from the data on dissociation energies by Chervonnyi,[29] disagree with our values. Unfortunately, in that report, the experimental and thermodynamic data used for the calculations were not given, so it is impossible to estimate the reliability of these values.

Charged vapor species
Mass spectra
In the thermal ionization (TI) mode, in the temperature range

Table 6. Enthalpies, $\Delta_s H°$ (kJ mol^{-1}), and entropies, $\Delta_s S°$ (J mol^{-1} K^{-1}), of sublimation

ΔT (K); N^a	II law[b]			III law[c]		Ref.
	$\Delta_s H°$ (T)	$\Delta_s S°$ (T)	$\Delta_s H°$ (298 K)	$\Delta_s H°$ (298 K)	$\Delta_s S°$ (T)	
			$[CeCl_3]^d = CeCl_3$			
959–1075; 19	303 ± 8	179.5 ± 8	327 ± 8	329 ± 10	183 ± 10	This work
			$\Delta_s H°$ (298 K) = 328 ± 6[e]			
1012–1071; 18	301 ± 13	178.5 ± 13	326 ± 13	328 ± 10	182 ± 10	18[f]
1450–1550	235 ± 4	123 ± 3	349 ± 4	321 ± 10	104.5 ± 10	17[f]
1143–1223; 4	177 ± 55	79 ± 46	264 ± 55	318 ± 10	125 ± 10	19[f]
876–1088; 45			326.0 ± 10.3	332.8 ± 6.2		10
			$2[CeCl_3] = Ce_2Cl_6$			
996–1075; 14	418 ± 20	218 ± 19	455 ± 20	451 ± 25	217 ± 25	This work
			$\Delta_s H°$ (298 K) = **453 ± 16**[e]			
1450–1550	235 ± 21	123 ± 16	443 ± 21	400 ± 25	68 ± 25	17[f]
1037–1091; 12				422.5 ± 12.0[f]		10
			$[SmCl_3] = SmCl_3$			
958–1038; 14	227.5 ± 16	131 ± 16	305 ± 16	306 ± 10	132.5 ± 10	This work[g]
980–1074; 15	228.5 ± 10	132.5 ± 10	307.5 ± 10	306 ± 10	131 ± 10	This work[h]
			$\Delta_s H°$ (298 K) = **306 ± 6**[e]			
774–854; 5	185 ± 23	132 ± 10	200 ± 23	254 ± 10	198 ± 10	20[f]
1450–1550	217	122	328	302	105	17[f]
			$2[SmCl_3] = Sm_2Cl_6$			
972–1045; 8	280 ± 31	146 ± 31	425 ± 31	392 ± 25	113 ± 25	This work[g]
979–1110; 23	265 ± 20	122 ± 19	415 ± 20	400 ± 25	108 ± 25	This work[h]
			$\Delta_s H°$ (298 K) = **408 ± 12**[e]			
1450–1550	296	125	480	410	66	17[f]
			$3[SmCl_3] = Sm_3Cl_9$			
1068–1109; 4				468 ± 40		This work[g]

[a] Number of measurements.

[b] Statistical errors corresponding to 95% of the confidence interval are given with a ± sign.

[c] Overall uncertainties following the ± sign include the systematic errors in the Gibbs energy functions and in vapor pressure values.

[d] Here and later the compounds in the condensed phase are indicated in parentheses.

[e] Mean weighted values, accepted as recommended.

[f] The values are calculated with thermodynamic functions accepted in this work.

[g] 1st run.

[h] 2nd run.

1043–1227 K, negative ions were detected. The relative ion intensities (given in parentheses and corrected for isotopic distributions) are as follows: Cl$^-$ (14.9), CeCl$_4^-$ (100), Ce$_2$Cl$_7^-$ (2.8), Ce$_3$Cl$_{10}^-$ (0.4), $T = 1153$ K; Cl$^-$ (8.8), SmCl$_4^-$ (100), Sm$_2$Cl$_7^-$ (3.2), and Sm$_3$Cl$_{10}^-$ (0.9), $T = 1152$ K.

Intense ion currents of positive alkali metal ions, arising from traces of alkali metal compounds, were also observed. In this work, as in some previous investigations,[30,31] we could not avoid the registration of Cl$^-$ ions formed on the outer surface of the cell. The problems arising from the observation of the non-equilibrium Cl$^-$ ions are described elsewhere.[31]

Ion-molecule reactions

To determine the enthalpies of formation of negative ions, various ion-molecule reactions have been studied. Using the measured ion currents as the basis, the equilibrium constants for the reactions, $K°_p$, were determined by using the relationship:

$$P_{ion} \sim I_i M^{1/2} T^{1/2} / a_i \gamma_i \qquad (3)$$

and these values are listed in Table 11 together with the results of third-law calculations.

For two ion-molecule reactions (see Fig. 8), the tempera-

ture dependences of the equilibrium constants were obtained, and the second law values of the reaction enthalpies were also calculated.

The investigation of TmCl$_3$–CeCl$_3$ and TmCl$_3$–SmCl$_3$ systems was undertaken to eliminate reactions involving Cl$^-$. The thermodynamic functions of the ions (Tables 8 and 9) were computed in the rigid rotator-harmonic oscillator approximation on the basis of molecular parameters estimated by us (see Table 7). The formation enthalpies of ions were calculated by the combination of the reaction enthalpies with the formation enthalpies of [LnCl$_3$], TmCl$_4^-$, and TmCl$_3$, taken from Refs 26 and 8. The formation enthalpies of the same ions calculated from different ion-molecule reactions turned out to be in good agreement with each other. The values of the formation enthalpies are given in Table 10.

CONCLUSIONS

1. The neutral and charged species have been studied in the saturated vapor over CeCl$_3$ and SmCl$_3$. Monomer, dimer, and trimer (Sm$_3$Cl$_9$) molecules, and LnCl$_4^-$, Ln$_2$Cl$_7^-$, Ln$_3$Cl$_{10}^-$ (Ln = Ce, Sm) negative ions, were observed in the saturated vapor in the temperature range 958–1227 K.

Table 7. Molecular constants

Molecule/ion	Symmetry	Interatomic distance r(Ln-Cl) (nm)	Angle (°)	Vibration frequencies (cm^{-1})
CeCl$_3$	D$_{3h}$	0.258	120	335, 52, 319(2), 80(2)
SmCl$_3$	C$_{3v}$	0.252	112	337, 55, 323(2), 82(2)
Ce$_2$Cl$_6$	D$_{2h}$	0.258 (r_t)	∠Cl$_b$-Ce-Cl$_b$ = 76	353, 279, 115, 63, 23, 254, 98, 375, 170, 16, 376, 109, 259,
		0.277 (r_b)	∠Cl$_t$-Ce-Cl$_t$ = 112	90, 45, 331, 237, 84
Ce$_2$Cl$_6$ (Ref. 10)	D$_{2h}$	0.257 (r_t)	∠Cl$_b$-Ce-Cl$_b$ = 82.7	330, 323, 312, 238, 233, 236, 327, 198, 91, 91, 74, 64, 44,
		0.275 (r_b)	∠Cl$_t$-Ce-Cl$_t$ = 116.5	32, 42, 12, 53, 32
Sm$_2$Cl$_6$	D$_{2h}$	0.252 (r_t)	∠Cl$_b$-Sm-Cl$_b$ = 76	346, 267, 109, 60, 22, 250, 92, 364, 166, 16, 366, 108, 254,
		0.271 (r_b)	∠Cl$_t$-Sm-Cl$_t$ = 112	86, 41, 324, 232, 74
Sm$_3$Cl$_9$	D$_{3h}$	0.252 (r_t)	∠Cl$_b$-Sm-Cl$_b$ = 110	400(6), 350(4), 250(4), 100(6), 70(4), 50(2), 30(2), 10(2)
		0.271 (r_b)	∠Sm-Cl$_b$-Sm = 130	
CeCl$_4^-$	T$_d$	0.258		372(3), 354, 58(2), 58(3)
SmCl$_4^-$	T$_d$	0.252		374(3), 359, 61(2), 91(3)
Ce$_2$Cl$_7^-$	D$_{3d}$	0.258	∠Cl-Ln-Cl = 112	517, 394(4), 307(2), 133(3), 96(5), 53(3), 17(2)
Sm$_2$Cl$_7^-$	D$_{3d}$	0.252	∠Cl-Ln-Cl = 112	520, 399(4), 314(2), 136(3), 102(5), 56(3), 18(2)
Ce$_3$Cl$_{10}^-$	D$_{3h}$	0.258 (r_t)	∠Cl$_b$-Ce-Cl$_b$ = 110	400(6), 350(3), 300(2), 250(3), 110(5), 75(5), 50(3), 30(4),
		0.277 (r_b)	∠Ce-Cl$_b$-Ce = 130	10(2)
Sm$_3$Cl$_{10}^-$	D$_{3h}$	0.252 (r_t)	∠Cl$_b$-Sm-Cl$_b$ = 110	400(6), 350(3), 300(2), 250(3), 110(5), 75(5), 50(3), 30(4),
		0.271 (r_b)	∠Sm-Cl$_b$-Sm = 130	10(2)

Notes. The interatomic distances r_b(Ln-Cl) in the dimer molecules Ln$_2$Cl$_6$ were accepted as 1.075 r_t(Ln-Cl) according to Ref. 23. The subscripts b and t correspond to bridge and terminal bonds, respectively.

The angles, ∠Cl$_t$-Ln-Cl$_t$ = 112° and ∠Cl$_b$-Ln-Cl$_b$ = 76°, were assumed to be equal to those in Al$_2$Cl$_6$.[16] Vibration frequencies of Ln$_2$Cl$_6$ molecules were estimated taking into consideration the trends of the available frequencies[16] in the order Al$_2$Cl$_6$, Ga$_2$Cl$_6$, In$_2$Cl$_6$. Molecular constants of LnCl$_4^-$, Ln$_2$Cl$_7^-$ ions, and the computation of the thermodynamic functions, were made by analogy with LaCl$_4^-$, La$_2$Cl$_7^-$ ions.[24] One frequency was not estimated for Ln$_2$Cl$_7^-$ ions due to hindered rotation being taken into consideration. Electronic partition functions were estimated to be nRln$g$, where $g = 2J + 1$, the statistical weight of the ground electronic state of Ln^{3+} ion (^{2}F$_{5/2}$ for Ce^{3+} and ^{6}H$_{5/2}$ for Sm^{3+} according to Ref. 25), J is the electronic moment of the Ln^{3+} ion, and n is the number of Ln atoms. The existence of excited electronic states was not taken into consideration. The thermodynamic functions of more complex molecules and ions were estimated by the comparison method on the basis of the thermodynamic functions from this work.

The number of equal frequencies is given in parentheses. The uncertainties in the Gibbs energy functions were estimated by the procedure described in Ref. 16 to be ± 8 (LnCl$_3$), ± 15 (LnCl$_4^-$), ± 25 (Ln$_2$Cl$_6$), ± 27 (Ln$_2$Cl$_7^-$), ± 35 (Sm$_3$Cl$_9$, Ln$_3$Cl$_{10}^-$), J·mol^{-1}·K^{-1}.

Table 8. Thermodynamic functions of gaseous species and the trichlorides in the condensed phase, $\Phi°(T)$/J·mol^{-1}·K^{-1} and $[H°(T)-H°(0)]$/kJ·mol^{-1}

T/K	$\Phi°(T)$	$H°(T)-H°(0)$	T/K	$\Phi°(T)$	$H°(T)-H°(0)$
	CeCl$_3$			SmCl$_3$	
298.15	306.08	19.24	298.15	310.64	19.17
1000	392.40	76.53	1000	396.77	76.44
1300	412.67	101.36	1300	417.03	101.27
	Ce$_2$Cl$_6$			Sm$_2$Cl$_6$	
298.15	444.02	38.96	298.15	448.42	39.35
1000	625.49	164.56	1000	630.97	165.09
1300	669.21	219.15	1300	674.81	219.69
	CeCl$_4^-$			Sm$_3$Cl$_9$	
298.15	324.86	23.76	298.15	570.51	57.43
1000	433.66	97.82	1000	842.89	250.19
1300	459.63	130.06	1300	909.49	334.41
	Ce$_2$Cl$_7^-$			SmCl$_4^-$	
298.15	498.94	42.28	298.15	323.44	23.67
1000	700.68	178.63	1000	431.99	97.70
1300	749.25	238.11	1300	457.93	129.93
	Ce$_3$Cl$_{10}^-$			Sm$_2$Cl$_7^-$	
298.15	613.86	63.98	298.15	494.21	43.16
1000	914.31	274.22	1000	694.98	182.32
1300	987.25	365.92	1300	743.45	243.04
	[CeCl$_3$]			Sm$_3$Cl$_{10}^-$	
298.15	81.91	20.60	298.15	614.10	63.98
1000	184.45	100.50	1000	914.55	274.22
1081	192.37	111.19	1300	987.48	365.92
1081	192.37	163.57		[SmCl$_3$]	
1300	220.44	198.83	298.15	81.38	20.49
			965	180.28	95.35
			965	180.28	149.85
			1000	185.81	155.10
			1300	226.34	200.10

Table 9. Values of the coefficients in Eqn ((3))

Molecule/Ion	a	b	c	d	e	f	g
$CeCl_3$	599.7941	91.4281	−0.004950	1.0577	−88.711	218.088	−266.394
$SmCl_3$	584.7207	84.2933	−0.002547	0.7543	−15.164	43.298	−58.959
Ce_2Cl_6	1020.3177	180.3430	−0.005334	1.8579	31.494	−89.368	124.230
Sm_2Cl_6	1043.9978	186.5285	−0.006709	2.0373	−41.946	110.314	−141.722
Sm_3Cl_9	1459.0145	281.8342	−0.011058	3.3994	−3.327	33.719	−69.210
$CeCl_4^-$	644.1716	98.0420	−0.000630	0.6788	109.474	−278.771	356.261
$SmCl_4^-$	675.1658	109.9120	−0.004434	1.1894	−19.202	41.243	−37.924
$Ce_2Cl_7^-$	1141.7859	201.2869	−0.006853	2.1257	22.897	−56.540	77.256
$Sm_2Cl_7^-$	1132.1288	199.9204	−0.006525	2.1092	33.867	−71.145	75.183
$Ce_3Cl_{10}^-$	1591.8176	308.8115	−0.012226	3.6090	−17.281	48.748	−64.441
$Sm_3Cl_{10}^-$	1576.6671	303.0817	−0.010124	3.3494	40.358	−85.636	92.840

**Table 10.** Enthalpies of formation of molecules and ions

Molecule	$\Delta_f H°$ (298 K)(kJ mol^{-1})	Ion	$\Delta_f H°$ (298 K)(kJ mol^{-1})
$CeCl_3$	−730 ± 6	$CeCl_4^-$	−1250 ± 15
$SmCl_3$	−722 ± 6	$SmCl_4^-$	−1252 ± 15
Ce_2Cl_6	−1663 ± 16	$Ce_2Cl_7^-$	−2184 ± 35
Sm_2Cl_6	−1649 ± 13	$Sm_2Cl_7^-$	−2172 ± 26
Sm_3Cl_9	−2617 ± 40	$Ce_3Cl_{10}^-$	−3183 ± 43
		$Sm_3Cl_{10}^-$	−3147 ± 43

Table 11. Equilibrium constants and the third law values of enthalpies of ion-molecule reactions, $\Delta_r H°$ (298 K)/kJ mol^{-1}

Reaction	$\ln K°_p$, T (K)	$\Delta_r H°$ (298 K)(kJ mol^{-1})
$Ce_2Cl_7^- = CeCl_4^- + [CeCl_3]^a$	3.79, 1129; 3.67, 1141; 3.51, 1167; 3.40, 1196; 3.47, 1215; 3.58, 1197; 3.47, 1186; 3.42, 1180; 3.38, 1204; 3.55, 1210; 3.34, 1227; 3.49, 1211; 3.72, 1144; 3.699, 1128; 3.82, 1118	−121 ± 34
$Ce_3Cl_{10}^- = CeCl_4^- + 2[CeCl_3]$	6.34, 1141; 5.52, 1153; 5.67, 1182; 6.19, 1128; 5.77, 1145; 6.16, 1163; 6.15, 1181; 6.33, 1174; 5.68, 1162	−182 ± 43
$Ce_3Cl_{10}^- = Ce_2Cl_7^- + [CeCl_3]$	2.09, 1141; 1.94, 1153; 2.62, 1182; 2.60, 1128; 2.04, 1145; 2.71, 1163; 2.66, 1181; 2.67, 1174; 2.09, 1162	−61 ± 50
$Sm_2Cl_7^- = SmCl_4^- + [SmCl_3]^b$	3.56, 1119; 3.64, 1132; 3.52, 1144; 3.81, 1141; 3.84, 1133; 3.81, 1111; 4.07, 1095; 4.00, 1084; 4.04, 1064; 3.74, 1043	−111 ± 34
$Sm_3Cl_{10}^- = SmCl_4^- + 2[SmCl_3]$	6.67, 1107; 4.44, 1095	−164 ± 43
$Sm_3Cl_{10}^- = Sm_2Cl_7^- + [SmCl_3]$	1.49, 1095	−51 ± 50
$TmCl_4^- + CeCl_3 = CeCl_4^- + TmCl_3$	1.08, 1011; −1.67, 1063; −2.95, 1075; −0.74, 1093; −0.61, 1105; −1.64, 1122; −1.70, 1144; −1.72, 1162; −1.68, 1175; −1.46, 1193	23 ± 15
$TmCl_4^- + SmCl_3 = SmCl_4^- + TmCl_3$	−0.87, 1039; −1.17, 1045	18 ± 15

[a] The second law values: $\Delta_r H°$ (1184 K) = −42 ± 14 kJ mol^{-1}, $\Delta_r H°$ (298 K) = −124 ± 13 kJ mol^{-1}. The mean weighted value obtained by the second and third laws, $\Delta_r H°$ (298 K) = −124 ± 13 kJ mol^{-1}, was accepted.
[b] The second law values: $\Delta_r H°$ (1106 K) = −28 ± 39 kJ mol^{-1}, $\Delta_r H°$ (298 K) = −106 ± 39 kJ mol^{-1}. The mean weighted value, $\Delta_r H°$ (298 K) = −109 ± 26 kJ mol^{-1}, was accepted.
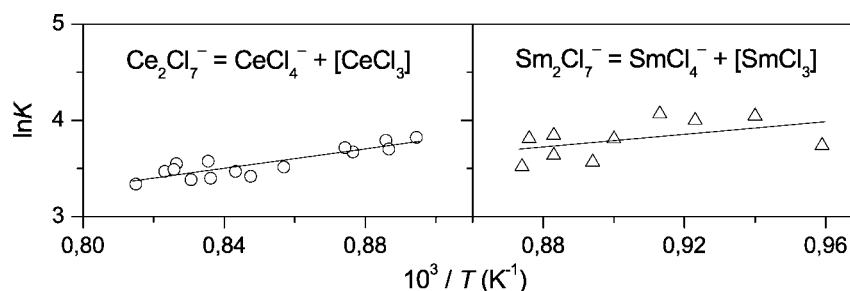
Figure 8. Temperature dependences of the equilibrium constants of ion-molecule reactions.

2. Partial vapor pressures of neutral constituents were determined, and the enthalpies of sublimation to monomers and associated molecules obtained.

3. Equilibrium constants for various chemical reactions were measured and the enthalpies of reactions were obtained using the second and third laws of thermodynamics.

4. The enthalpies of formation of molecules and ions in the gaseous phase have been calculated.

Acknowledgement

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