Research Article

Study of Molecular and Ionic Vapor Composition over CeI$_3$ by Knudsen Effusion Mass Spectrometry

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The molecular and ionic composition of vapor over cerium triiodide was studied by Knudsen effusion mass spectrometry. In the saturated vapor over CeI$_3$ the monomer, dimer, and trimer molecules and the negative ions I$^-$, CeI$_4{}^-$, and Ce$_2$I$_7{}^-$ were identified in the temperature range of 753–994 K. The partial pressures of CeI$_3$, Ce$_2$I$_6$, and Ce$_3$I$_9$ were determined and the enthalpies of sublimation, $\Delta_s H°(298.15\,\text{K})$ in kJ·mol^{-1}, in the form of monomers (298 ± 9), dimers (415 ± 30), and trimers (423 ± 50) were obtained by the second and third laws of thermodynamics. The enthalpy of formation, $\Delta_f H°(298.15\,\text{K})$ in kJ·mol^{-1}, of the CeI$_3$ (−371 ± 9), Ce$_2$I$_6$ (−924 ± 30), and Ce$_3$I$_9$ (−1585 ± 50) molecules and the CeI$_4{}^-$ (−857 ± 19) and Ce$_2$I$_7{}^-$ (−1451 ± 50) ions were calculated. The electron work function, $\varphi_e = 3.3 ± 0.3$ eV, for the CeI$_3$ crystal was evaluated.

1. Introduction

Vaporization thermodynamics of cerium triiodide is the focus of researcher's attention so far. The first measurements of vapor pressure over CeI$_3$ were carried out by Knudsen effusion mass spectrometry (KEMS) [1] and Knudsen effusion Cahn microbalance [2] techniques. Further KEMS studies were performed by Chantry [3, 4], Struck and Feuersanger [5], and Ohnesorge [6]. In addition the vapor pressure of CeI$_3$ was determined by the torsion method [7], by optical absorption spectra [8], and recently by X-ray induced fluorescence [9]. In spite of the numerous experimental results [1–9], data on the vapor composition over CeI$_3$ are very scanty. Moreover, information on the ionic species in saturated vapor over CeI$_3$ is absent so far.

The present work continues our systematic investigations of the molecular and ionic sublimation of lanthanide halides by KEMS; see for example, [10–14]. The composition of the saturated vapor of CeI$_3$ was determined and the thermochemical data of the vapor constituents were refined on the basis of the latest sets of molecular parameters.

2. Experimental

A single-focusing magnetic sector type mass spectrometer MI1201 modified for high-temperature studies was used. The combined ion source allowed carrying out successive measurements in two modes; see Figure 1 (taken from [15]). In addition to a standard mode of electron ionization (EI) for analysis of neutral vapor species, a thermal ion emission (TE) mode was introduced for the analysis of charged vapor constituents formed inside an effusion cell as a result of thermal ionization. In the latter case, the ions are drawn out from the cell by a weak electric field (10^4–10^5 V/m) applied between the cell and the collimator (1). The sample (2) was placed into a molybdenum cell (3) under dry conditions in a glove box and then transferred into the vaporization chamber of the mass spectrometer and evacuated. The lid of the cell had the cylindrical effusion orifice (Ø 0.3 × 0.8 mm). The vaporization-to-effusion area ratio was about 400. A resistance furnace was used for the heating of the cell. Its temperature was measured by a tungsten-rhenium thermocouple calibrated with silver to a ±5 K accuracy in the separate experiment.
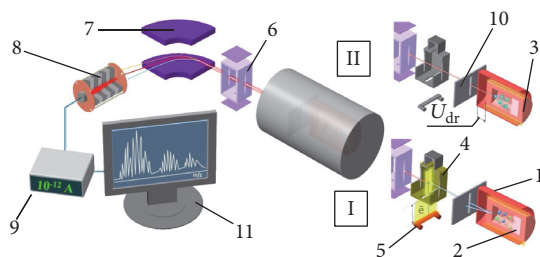
Figure 1: Scheme of the mass spectrometer (taken from [15]). I—EI mode; II—TE mode. The details are given in text.

Figure 2: Temperature dependence of the mass spectra of CeI_3. Heating and cooling runs are marked by solid and open symbols, respectively.

The vapor species effusing from the cell form a molecular beam, which reaches the ionization chamber (4) and intersects with an electron beam of specified energy. The ionization voltage U_e is set by a computer using a programmable power supply AKIP-1125 in the range of 0–150 V with 10 mV resolution. The tungsten ribbon-type cathode (5) is directly heated by an controllable DC source. The current of the cathode was adjusted to provide a constant emission current of 0.25 A.

The ions formed by the collision of molecular species with electrons are extracted from the ionization chamber, focused, and accelerated by a system of electrostatic lenses (6). The electrostatic capacitor mounted after the exit slit of the ion source allows us to study the distribution of ions by the vertical velocity component. The accelerating voltage (3 kV) is applied to the ionization chamber (IE mode) or to the effusion cell (TE mode). The polarity of the high voltage can be reversed with respect to the ground potential. Thus, both positive and negative ions can be analyzed. The ions are separated according to their mass-to-charge ratio in the magnetic field of an electromagnet (7) (90°, 200 mm curvature radius). The magnetic field strength is measured by a Hall probe. The ion current registration system (8, 9) includes a secondary electron multiplier Hamamatsu R595 (8) and a Picoammeter Keithley 6485 with 10 fA resolution and 20 fA typical noise. It allows measuring ion currents down to 10^{-18} A. The movable shutter (10) operated by a computer (11) allows distinguishing signals caused by the effusing species from those of the background. The special software "HTMSLab" was used to control experimental parameters, collect and process the data, and export the results into the database. Further details on the apparatus and experimental procedure can be found elsewhere [16–18].

The cerium triiodide sample was synthesized from cerium metal (99.9%, Metall Rare Earth Ltd.) and iodine (p.a., sublimed, Merck). The elements were sealed in an evacuated silica ampoule and slowly heated to 750°C until the reaction was completed. Afterwards the product was sublimed for purification in a sealed silica ampoule under vacuum at 750°C, that is, slightly below the melting point of CeI_3 at 766°C. The bright yellow CeI_3 is very hygroscopic. Its synthesis was performed under strictly oxygen-free and anhydrous conditions.
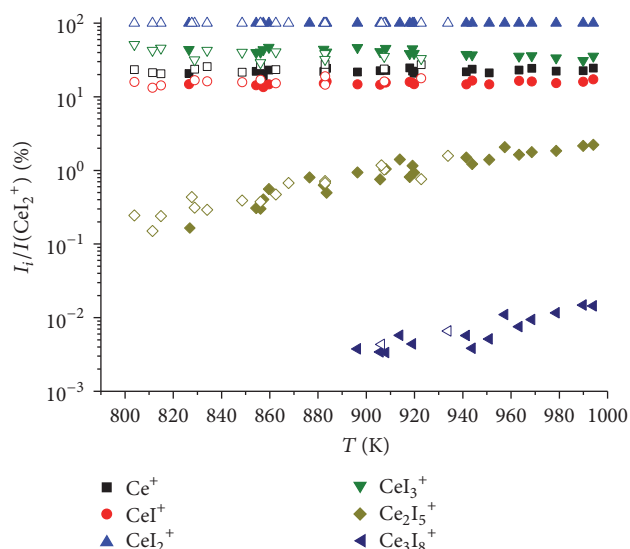
3. Results and Discussion

3.1. Neutral Vapor Species. In the IE mass spectra of the saturated vapor over cerium triiodide the $Ce^+(23)$, $CeI^+(16)$, $CeI_2^+(100)$, $CeI_3^+(31)$, $Ce_2I_3^+(0.02)$, $Ce_2I_4^+(0.01)$, $Ce_2I_5^+(2.2)$, $I^+(22)$, and $Ce_3I_8^+(0.02)$ ions, as well as the doubly charged $Ce^{++}(0.5)$, $CeI^{++}(7)$, and CeI_2^{++} (3) ions, were registered in the temperature range of 753–994 K. The relative ion currents are given in parentheses for the temperature of 990 K and the energy of ionizing electrons of 40 eV. The mass spectra were found to be constant over the whole evaporation time; see Figure 2.

To determine the molecular precursors of the ions, the ionization efficiency curves (IEC) (Figure 3) and the temperature dependencies of ion currents (Figure 4) were analyzed. The ionizing electron energy in Figure 3 was corrected by the background signal of HI^+ (AE = 10.38 eV [19]). Appearance energies (AE) were determined by vanishing current (VC) and linear extrapolation (LE) methods; average values are given in Table 1. The linear part for the LE method was determined as the segment between two points of inflection on the first-order derivative of the IEC inverse function [20]. The following conclusions were drawn: the ions containing one atom of cerium are formed as a result of direct (CeI_3^+) and dissociative (Ce^+, CeI^+, and CeI_2^+) ionization of the monomer CeI_3 molecules with negligibly small contributions from the fragmentation of more complex molecules; the $Ce_2I_3^+$, $Ce_2I_4^+$, and $Ce_2I_5^+$ ions were produced by the dissociative ionization of the dimer Ce_2I_6 molecules; and the $Ce_3I_8^+$ ion originated from the trimer molecule Ce_3I_9.

Along with the abovementioned ions I^+ was also observed. The determined AE equal to 10.7 ± 0.5 eV (Table 1) points out its origination from atomic iodine (ionization energy $IE(I)$ = 10.4 eV [21]), which can be attributed to the partial decomposition of the sample with the formation of

TABLE 1: Ion appearance energies (eV).

Reaction	Ion	AE				
		This work	[1]	[3]	[5]	[30]
$CeI_3 + \bar{e} = Ce^+ + 3I + 2\bar{e}$	Ce^+	17.2 ± 0.5	17.7 ± 0.5	16.75 ± 0.15		
$CeI_3 + \bar{e} = CeI^+ + 2I + 2\bar{e}$	CeI^+	13.1 ± 0.5	13.6 ± 0.5	13.15 ± 0.15		
$CeI_3 + \bar{e} = CeI_2^+ + I + 2\bar{e}$	CeI_2^+	9.8 ± 0.5	9.7 ± 0.5	9.55 ± 0.1	11.2	
$CeI_3 + \bar{e} = CeI_3^+ + 2\bar{e}$	CeI_3^+	9.1 ± 0.5	9.6 ± 0.5	9.05 ± 0.1	10.8	9.71
$Ce_2I_6 + \bar{e} = Ce_2I_5^+ + I + 2\bar{e}$	$Ce_2I_5^+$	9.3 ± 0.5				
$Ce_3I_9 + \bar{e} = Ce_3I_8^+ + I + 2\bar{e}$	$Ce_3I_8^+$	9.1 ± 0.5				
$I + \bar{e} = I^+ + 2\bar{e}$	I^+	10.7 ± 0.5	~13.5	10.5		
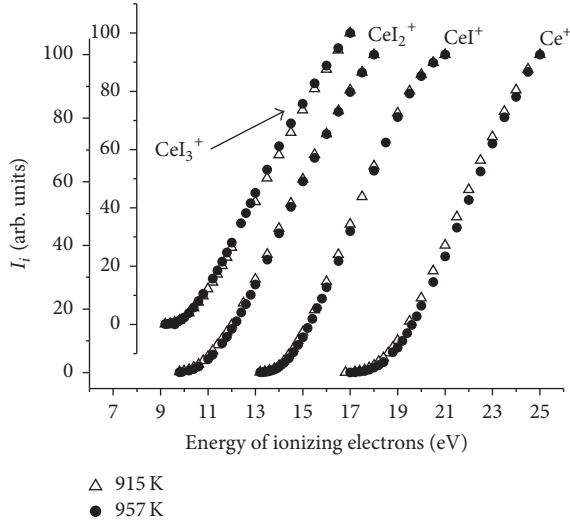
(a)
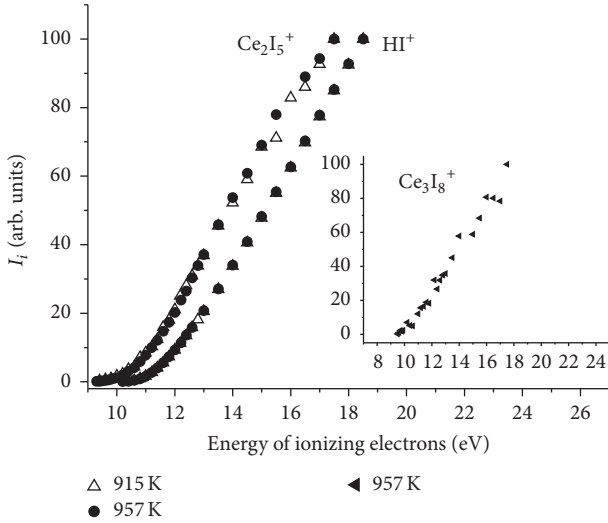
(b)

FIGURE 3: Ionization efficiency curves.

FIGURE 4: Temperature dependence of ion currents in the EI regime.

CeI$_2$. Nevertheless the reproducibility of the mass spectra in heating and cooling cycles (Figure 2), the shapes of IECs showing no brakes, and the determined AE values (Table 1) indicate unambiguously the absence of CeI$_2$ in the vapor. This fact agrees with the expected much lower volatility of CeI$_2$

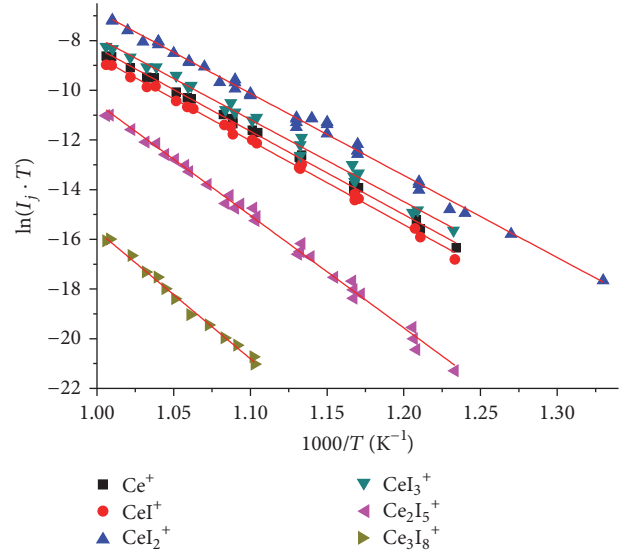compared to that of CeI$_3$ in the studied temperature range. Therefore it is assumed that the activity of CeI$_3$ in the solid state was unity.

The partial pressures of molecules (p_j) (see Table 2) were calculated according to the conventional KEMS procedure using the equation

$$p_j = \frac{k \cdot I \cdot T}{\sigma_j}, \quad (1)$$

where k is the sensitivity constant of mass spectrometer (determined in a separate experiment with Ag; the vapor pressure of silver was taken from [22]), σ_j is the ionization cross section of the jth molecule at the working energy of the ionizing electrons (calculated from the experimentally determined atomic cross sections, σ_{at} [23, 24], by the equation $\sigma_j = 0.75\Sigma\sigma_{at}$ [25]), $I_j = \sum_i (I_{ij}/(a_i \cdot \gamma_i))$ is the total ion current of the ith ion species formed from the jth molecule, a_i is the natural abundance of the measured isotope of the ith ion, γ_i is the ion-electron conversion coefficient of secondary electron multiplier for the ith ion ($\gamma_i \sim M^{-1/2}$ [26], where M is the mass of ion), and T is the temperature of the cell.

TABLE 2: Partial pressures (Pa) of the molecules.

CeI$_3$		Ce$_2$I$_6$		Ce$_3$I$_9$	
T, K	$p_j \cdot 10^3$	T, K	$p_j \cdot 10^4$	T, K	$p_j \cdot 10^5$
885	54.5	878	3.59	916	0.85
872	47.8	915	26.8	957	7.45
877	55.4	957	182	932	1.83
877	54.7	933	57.0	907	0.41
914	235	906	14.3	905	0.65
957	1080	866	1.62	921	0.84
934	445	829	0.15	945	4.29
906	150	857	1.27	952	5.24
868	29.8	882	5.80	962	12.5
828	4.32	906	17.0	978	29.9
786	0.52	920	39.8	992	58.1
805	1.23	946	134	907	0.51
753	0.081	853	0.76	923	1.08
872	43.5	952	170	943	2.74
957	1210	963	323	969	15.3
857	20.3	978	566	994	54.2
882	59.5	992	1010		
906	145	907	23.9		
919	274	923	28.8		
942	575	883	4.19		
854	15.8	857	0.90		
951	786	829	0.20		
963	1280	811	0.035		
979	1970	828	0.081		
990	3020	857	0.64		
908	150	884	3.77		
923	244	917	24.0		
883	40.1	943	105		
856	15.5	969	343		
829	4.06	994	999		
811	1.48				
826	3.24				
856	13.7				
883	48.8				
918	189				
944	551				
969	1250				
994	2880				

TABLE 3: Coefficients of (2).

Species	T, K	A	B
CeI$_3$	753–994	33.35 ± 0.36	34.84 ± 0.41
Ce$_2$I$_6$	811–994	44.93 ± 0.62	43.10 ± 0.69
Ce$_3$I$_9$	905–994	49.62 ± 1.43	42.43 ± 1.52

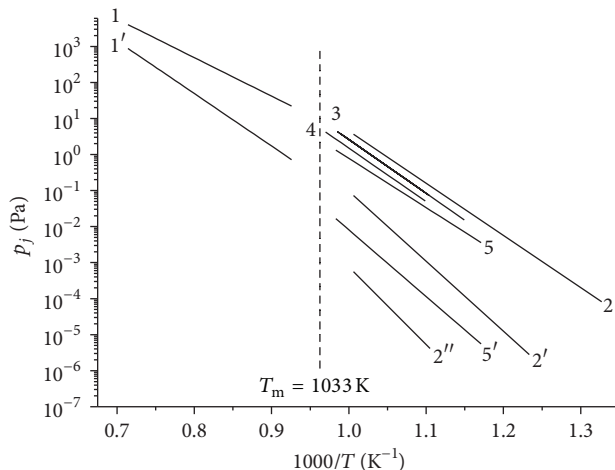The standard deviation is given with a "$\pm$" sign.

FIGURE 5: Temperature dependencies of the saturated vapor pressure: (1) $p(\text{CeI}_3)$ from [9], (2) our data, (3) [2], (4) [7], and (5) [6]; (1$'$) $p(\text{Ce}_2\text{I}_6)$ from [9], (2$'$) our data, and (5$'$) [6]; (2$''$) $p(\text{Ce}_3\text{I}_9)$ our data.

The temperature dependence of the saturated vapor pressures of the monomer and oligomer molecules was approximated by the equation

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

The coefficients of equation (2) are given in Table 3.

The partial pressures of the molecules of cerium triiodide from different references are compared in Figure 5. As one can see, all experimental vapor pressure values are scattered within about one order of magnitude. Temperature dependencies from the work of Hirayama et al. [2], Villani et al. [7], and Ohnesorge [6] lie below those obtained in this work. The fraction of the dimer molecules measured in this work and in [6] is about the same whereas the absolute pressures differ considerably. The vapor pressure of trimer molecules was determined in this study for the first time.

The enthalpies and entropies of sublimation of cerium triiodide in the form of monomer and oligomer molecules were determined from the temperature dependencies of the partial pressures of the saturated vapor species using the procedure for experimental data processing according to the second and third laws of thermodynamics; see Table 4. The thermodynamic functions required for calculations were taken from [22] for CeI$_{3,\text{cr}}$ and evaluated in this work for the monomer and oligomer molecules in the state of an ideal gas (see Appendix).

As it is seen from Table 4, the values of $\Delta_s H^\circ(298.15)$ and $\Delta_s S^\circ(T)$ obtained in this work by the second and third laws are in a fair agreement for both monomer and oligomer molecules. The same can be said about the results for the monomer molecules from [2, 7]. The data of the work [9] are in notably worse agreement, whereas those of [6, 8] do not agree within the given uncertainties. At the same time, the third law values for all the data are in a good consent with each other. The temperature trend of the third law values $\Delta_s H^\circ(298.15)$ is given in Figure 6, from which one can see that the data of this work and [2, 9] do not show a pronounced temperature dependence as compared to those of [6, 7]. Taking into account this analysis, the recommended values

TABLE 4: Enthalpies, $\Delta_s H°$ (kJ·mol^{-1}), and entropies, $\Delta_s S°$ (J·mol^{-1}·K^{-1}), of sublimation of cerium triiodide.

ΔT, K	T, K	N[1]	II law[2]			III law[3]		Ref.
			$\Delta_{s,v}H°(T)$	$\Delta_{s,v}S°(T)$	$\Delta_s H°(298)$	$\Delta_s H°(298)$	$\Delta_{s,v}S°(T)$	
				$CeI_{3,cr,l} = CeI_{3,g}$				
753–994	893	38	277 ± 3	194 ± 3	292 ± 4	294 ± 10	191 ± 10	This work
?	933	?	292 ± 21		307 ± 21			[1]
870–1015	945	32	284 ± 4	197 ± 4	301 ± 4	298 ± 10	189 ± 10	[2]
810–953	877	50	274 ± 2		288 ± 2			[5]
854–1017	936	29	284 ± 1	164 ± 1	278 ± 1	307 ± 10	189 ± 10	[6]
910–1031	970	81	284 ± 3	192 ± 6	301 ± 3	303 ± 10	189 ± 10	[7]
	1000	1				291 ± 10	187 ± 10	[8]
1072–1136	1094	5	201 ± 11	119 ± 10	272 ± 11	296 ± 10	155 ± 10	[8]
1080–1400	1250	?	299 ± 1	119 ± 1	290 ± 1	301 ± 10	123 ± 10	[9]
						297		[22]
						322		[27]
						280		[28]
						300 ± 5		[29]
				$\Delta_s H°(298.15\,K) = \mathbf{298 ± 9}$[4]				
				$2CeI_{3,cr,l} = Ce_2I_{6,g}$				
811–994	893	30	374 ± 6	262 ± 6	395 ± 25	409 ± 30	278 ± 30	This work
825–953	898	50	377 ± 5		400 ± 15			[5]
854–1017	936	17	354 ± 1	219 ± 1	379 ± 25	428 ± 30	276 ± 30	[6]
1080–1400	1250	?	251 ± 1	138 ± 1	413 ± 1	421 ± 30	148 ± 30	[9]
				$\Delta_s H°(298.15\,K) = \mathbf{415 ± 30}$				
				$3CeI_{3,cr} = Ce_3I_{9,g}$				
907–994	949	16	413 ± 12	257 ± 13	443 ± 40	423 ± 50	236 ± 50	This work
				$\Delta_s H°(298.15\,K) = \mathbf{423 ± 50}$				

[1] Number of measurements.
[2] The original errors are given for the literature data, the standard deviations for this work.
[3] The uncertainties are mainly determined by those in thermodynamic functions.
[4] The uncertainty of the recommended values was calculated by Student's method (monomer) and accepted as the third law ones (others).
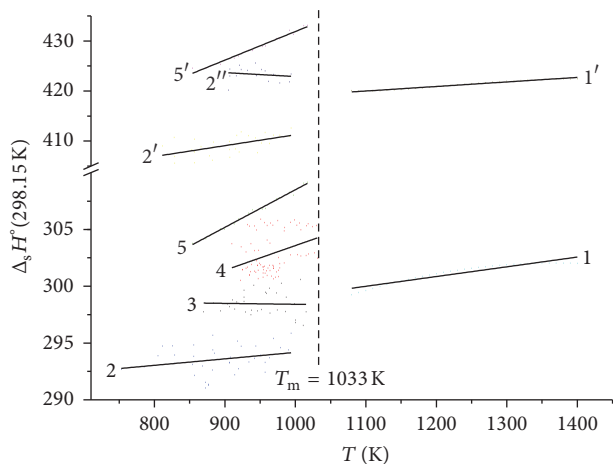
FIGURE 6: Temperature dependencies of the third law $\Delta_s H°(298.15\,K)$ values: (1) monomer from [9], (2) our data, (3) [2], (4) [7], and (5) [6]; (1′) dimer from [9], (2′) our data, and (5′) [6]; (2″) trimer our data.

were selected and emphasized in bold in Table 4. The early estimates [27, 28] made for monomers differ considerably from the recommended value, while the assessments given in [22, 29] agree with the experimental data.

The standard formation enthalpies, $\Delta_f H°(298.15\,K)$, are equal to $-371 ± 9$ kJ·mol^{-1} (CeI_3), $-924 ± 30$ kJ·mol^{-1} (Ce_2I_6), and $-1585 ± 50$ kJ·mol^{-1} (Ce_3I_9) and were calculated from the recommended $\Delta_s H°(298.15\,K)$ values. The formation enthalpy of crystalline cerium triiodide, $\Delta_f H°(CeI_{3,cr};\ 298.15\,K) = -669$ kJ·mol^{-1} [22], was used.

3.2. Charged Vapor Species. In the TE mass spectra in the temperature range of 747–960 K the I$^-$ (0.44), CeI_3^- (0.18), CeI_4^- (100), and $Ce_2I_7^-$ (0.08) ions were identified with the relative ion currents given in parentheses for $T = 846$ K.

Additional experiments with the CeI_3-PrI_3 binary system were performed to determine the enthalpy of formation of CeI_4^- ions. The enthalpy of exchange ion-molecular reaction (5) was found to be $1 ± 5$ kJ·mol^{-1}. The enthalpy of formation of PrI_4^- $\Delta_f H°(298.15\,K) = -860 ± 23$ kJ·mol^{-1} was used as reference value. It was obtained by recalculation of the data ($-865 ± 25$ kJ·mol^{-1}) [13] with the thermodynamic function used in this work. The experimental equilibrium constants of reaction (3) and reaction (4) investigated over pure CeI_3 are listed in Table 5:
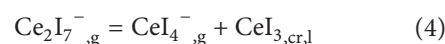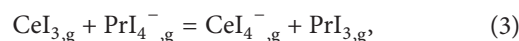
$$CeI_{3,g} + PrI_{4^-,g} = CeI_{4^-,g} + PrI_{3,g}, \tag{3}$$

$$Ce_2I_{7^-,g} = CeI_{4^-,g} + CeI_{3,cr,l} \tag{4}$$

TABLE 5: Experimental data for reactions (3) and (4).

	Reaction (3)		Reaction (4)
T (K)	$\ln K_P^{\circ}$	T (K)	$\ln K_P^{\circ}$
889	0.35	868	6.39
865	0.39	862	6.61
835	0.30	898	5.92
846	0.49	932	5.43
907	0.41	960	4.94
934	0.39	924	5.49
966	0.38	892	5.94
956	0.37	846	6.67
929	0.34		
906	0.22		
856	0.34		
806	0.38		
854	0.30		
884	0.38		
902	0.30		
950	0.40		
976	0.30		

The reaction enthalpies were calculated by the second and third laws of thermodynamics; see Table 6. The evaluation of the thermodynamic functions of the CeI_4^- and $Ce_2I_7^-$ ions is described in Appendix.

One can see that the agreement for the enthalpy of reaction (3) obtained by the second and third laws is good. $\Delta_f H^{\circ}(CeI_4^-, 298.15\,K) = -857 \pm 19\,kJ\cdot mol^{-1}$ was recommended. This value is in agreement with those $-850 \pm 33\,kJ\cdot mol^{-1}$ obtained by Chantry from the enthalpy of the reaction $CeI_4^-{}_{,g} = I^-{}_{,g} + CeI_{3,g}$ and recalculated with our sublimation enthalpy and thermodynamic functions. The selected formation enthalpy of the $Ce_2I_7^-$ ion is $-1451 \pm 50\,kJ\cdot mol^{-1}$ (third law) and was obtained for the first time.

3.3. Thermodynamic Properties Derived from IECs.

The enthalpies of ion-molecular reactions were calculated from the differences of the measured AE values given in Table 1; see Table 7. On their basis the standard formation enthalpies of the ions were determined; see Table 8. The accurate values of $\Delta_f H^{\circ}(Ce^+, 298.15\,K) = 957 \pm 0.1\,kJ\cdot mol^{-1}$ [22] and $\Delta_f H^{\circ}(I, 298.15\,K) = 106.76 \pm 0.04\,kJ\cdot mol^{-1}$ [22] and the formation enthalpies of the CeI_3, Ce_2I_6, and Ce_3I_9 molecules obtained in this work (see above) were used as references. The comparison of our results with the data obtained by photoelectron spectroscopy [30], computation [31], and assessment [32] shows that all data are in agreement within the given errors; see Table 8.

Analysis of the ion-molecular reaction enthalpies confirmed the weakness of the first cerium iodine bond in comparison with the other two. Probably, it explains the lower enthalpy of the formation of CeI_2^+ ($467 \pm 10\,kJ\cdot mol^{-1}$) compared to CeI_3^+ ($497 \pm 10\,kJ\cdot mol^{-1}$).

The formation enthalpy of gaseous CeI_3 ($-371 \pm 9\,kJ\cdot mol^{-1}$) obtained from the vapor pressure measurement is in a good agreement with those calculated from the appearance energies ($-376 \pm 50\,kJ\cdot mol^{-1}$) and with the value ($-381\,kJ\cdot mol^{-1}$) assessed by Sapegin et al. [33] (Table 9). The coincidence of the formation enthalpy values of $CeI_{3,g}$, as determined from the thermodynamic and threshold approaches, points out a negligible contribution from the excitation and kinetic energy of the fragments. The atomization energy derived from $\Delta_f H^{\circ}(CeI_3, 298.15\,K) = -371 \pm 9\,kJ\cdot mol^{-1}$ was found to be $1109 \pm 10\,kJ\cdot mol^{-1}$. It yields the average bond strength equal to $370 \pm 10\,kJ\cdot mol^{-1}$.

3.4. Electron Work Function.

The mass spectrometric approach for the work function determination is based on the use of thermochemical cycles including desorption enthalpies of ions and sublimation enthalpies of molecules as described elsewhere [34]. The desorption enthalpy of the CeI_4^- ions, $\Delta_{des}H^{\circ}(851\,K) = 350 \pm 8\,kJ\cdot mol^{-1}$, and the $Ce_2I_7^-$ ions, $\Delta_{des}H^{\circ}(902\,K) = 430 \pm 18\,kJ\cdot mol^{-1}$, were obtained from the temperature dependence of their ion currents; see Figure 7. The electron work function was calculated in accordance with the following expressions:

$$\varphi_e = -\frac{1}{4}D(CeI_3) + \frac{5}{4}\cdot\Delta_s H^{\circ}(CeI_3) + EA(I) + \Delta_{diss}H^{\circ}(CeI_4^-) + \Delta_{des}H^{\circ}(CeI_4^-), \tag{5}$$

$$\varphi_e = -\frac{1}{4}D(CeI_3) + \frac{9}{4}\cdot\Delta_s H^{\circ}(CeI_3) + EA(I) + \Delta_{diss}H^{\circ}(Ce_2I_7^-) + \Delta_{des}H^{\circ}(Ce_2I_7^-), \tag{6}$$

where EA(I) is the electron affinity of iodine [22], $D(CeI_3)$ is the dissociation enthalpy of the CeI_3 molecule, $\Delta_{diss}H^{\circ}(CeI_4^-)$ is the enthalpy of the $CeI_4^- = I^- + CeI_3$ reaction (Table 6), and $\Delta_{diss}H^{\circ}(Ce_2I_7^-)$ is the enthalpy of the $Ce_2I_7^- = I^- + 2CeI_3$ reaction.

The φ_e values equal to $3.3 \pm 0.3\,eV$ and $3.5 \pm 0.5\,eV$ were obtained from (5) and (6), respectively. They turned out to be close to $\varphi_e(LaI_3) = 3.5 \pm 0.3\,eV$ [14].

4. Conclusions

New experimental data on the saturated vapor composition of CeI_3 have been obtained by a Knudsen effusion mass spectrometer. The monomer, CeI_3, dimer, Ce_2I_6, and trimer, Ce_3I_9, molecules, as well as the $[I(CeI_3)_n]^-$ ions ($n = 0$–2), have been observed in the temperature range of 747–994 K. The Ce_3I_9 molecules and the $Ce_2I_7^-$ ions were detected for the first time. The sublimation enthalpies of the monomer and oligomer molecules were calculated by the second and third laws of thermodynamics. Critical analysis of all available data allowed us to recommend the following enthalpies of sublimation: $\Delta_s H^{\circ}(298.15\,K)$ in $kJ\cdot mol^{-1}$: 298 ± 9 (monomer), 415 ± 30 (dimer), and 423 ± 50 (trimer) and to calculate the formation enthalpies, $\Delta_f H^{\circ}(298.15\,K)$ in $kJ\cdot mol^{-1}$: -371 ± 9 (CeI_3), -924 ± 25 (Ce_2I_6), -1585 ± 50 (Ce_3I_9), -857 ± 19

TABLE 6: Enthalpies (kJ·mol^{-1}) of reactions (3) and (4).

ΔT, K	T, K	N[1]	II law[2]		III law[3]	Ref.
			$\Delta_r H°(T)$	$\Delta_r H°(298.15\,\text{K})$	$\Delta_r H°(298.15\,\text{K})$	
			$CeI_{3,g} + PrI_4{}^-{}_{,g} = CeI_4{}^-{}_{,g} + PrI_{3,g}$			
806–976	897	17	0 ± 3	1 ± 3	1 ± 5	This work
			$Ce_2I_7{}^-{}_{,g} = CeI_4{}^-{}_{,g} + CeI_{3,cr,l}$			
842–960	896	12	-99 ± 5	-113 ± 6	-75 ± 40	This work

[1] Number of measurements.
[2] The original errors are given for the literature data, the standard deviations for this work.
[3] The uncertainties are mainly determined by those in thermodynamic functions.

TABLE 7: Ion-molecular reactions (kJ·mol^{-1}).

Reaction	This work	[1]	[3]	[5]	[30]	[31]
$CeI^+{}_{,g} = Ce^+{}_{,g} + I_g$	391 ± 10	396 ± 50	347 ± 50			393
$CeI_2{}^+{}_{,g} = CeI^+{}_{,g} + I_g$	323 ± 10	376 ± 50	347 ± 50			
$CeI_3{}^+{}_{,g} = CeI_2{}^+{}_{,g} + I_g$	66 ± 10	10 ± 50	48 ± 50	39	62 ± 50	
$CeI_{3,g} + Ce_2I_5{}^+{}_{,g} = Ce^+{}_{,g} + 2I_g + Ce_2I_{6,g}$	750 ± 10					
$CeI_{3,g} + Ce_3I_8{}^+{}_{,g} = Ce^+{}_{,g} + 2I_g + Ce_3I_{9,g}$	768 ± 20					

TABLE 8: Ion formation enthalpies (kJ·mol^{-1}).

Ion	This work	[1]	[3]	[32]	[31]
CeI^+	673 ± 10	669 ± 50	717	760	671
$CeI_2{}^+$	467 ± 10	399 ± 50	476		
$CeI_3{}^+$	497 ± 10	496 ± 50	535		
$Ce_2I_5{}^+$	-131 ± 10				
$Ce_3I_8{}^+$	-811 ± 20				

TABLE 9: Formation enthalpies of $CeI_{3,g}$ (kJ·mol^{-1}).

This work from IEC	This work from $\Delta_s H°$	[1]	[9]	[33]
$>-376 \pm 50$	-371 ± 9	-436 ± 50	-349	-381

FIGURE 7: Temperature dependencies of $CeI_4{}^-$ and $Ce_2I_7{}^-$ ion currents.
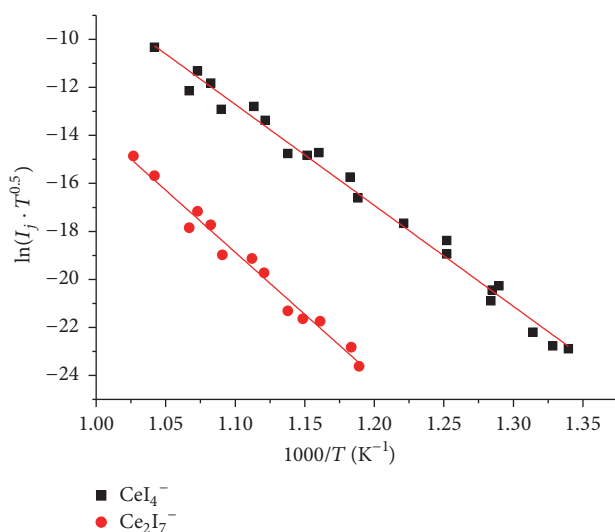
($CeI_4{}^-$), and -1451 ± 50 ($Ce_2I_7{}^-$). The electron work function for cerium triiodide (3.3 ± 0.3 eV) has also been evaluated.

Appendix

A. Description of the Used Thermodynamic Functions of Molecules and Ions

A.1. $CeI_{3,cr,l}$. The thermodynamic functions of CeI_3 in the solid and liquid state were taken from [22].

A.2. $CeI_{3,g}$. For the first time the thermodynamic functions of monomer molecules CeI_3 in the state of an ideal gas were evaluated by Myers and Graves [35] in the rigid rotator-harmonic oscillator (RRHO) approximation; these were included in the handbooks by Pankratz [36] and Barin [37]. Later the assessment of the functions was made by Osina et al. [38]; they can be found in the IVTANTHERMO database [22]. Recently Solomonik et al. [39] performed quantum-chemical calculations for $CeI_{3,g}$ at a multireference configuration interaction MRCISD+Q level of theory taking into account relativistic effects; a significant spin-orbit coupling effect on the molecular properties was revealed.

The data used in this work are based on those from [22] taking into account the low lying electronic states computed in [39].

A.3. $Ce_2I_{6,g}$. The thermodynamic functions of dimer molecules were calculated in the RRHO approximation using the molecular constants (symmetry D_{2h}) from [40]. The electronic contribution was taken as doubled compared with the monomers in accordance with [41].

TABLE 10: Coefficients of polynomial (A.4).

	T, K	$-a, 10^{-1}$	$b, 10^2$	$-c$	$d, 10^{-3}$	$-e, 10^{-3}$	$f, 10^{-4}$
$\mathrm{CeI_{3,cr,l}}$	0–1033	47.08	2.326	3.838	2.391	8.699	1.760
	1033–1500	106.9	26.03	16.90	1.830	3.165	0.289
$\mathrm{CeI_3}$	0–1500	110.0	1.489	4.011	3.480	12.77	2.158
$\mathrm{CeI_4^-}$	0–1500	122.9	1.780	4.748	4.156	15.36	2.604
$\mathrm{Ce_2I_6}$	0–1500	177.9	2.760	7.349	6.477	23.88	4.043
$\mathrm{Ce_2I_7^-}$	0–1500	27.52	16.59	20.47	4.390	9.010	0.966
$\mathrm{Ce_3I_9}$	800–1500	992.1	441.8	194.6	2.251	1.601	1.060

The errors in the functions of Gibbs energy estimated in this work are assumed to be equal to ±5 ($\mathrm{CeI_3}$), ±25 ($\mathrm{Ce_2I_6}$), ±40 ($\mathrm{Ce_2I_7^-}$), and ±50 ($\mathrm{Ce_3I_9}$) J mol^{-1} K^{-1}.

A.4. $Ce_3I_{9,g}$. The thermodynamic functions of trimers were assessed by the additive approach with an empiric correction based on the functions of the monomer and oligomer molecules of $\mathrm{LuCl_3}$ [42] using the following expressions:

$$\mathrm{TDF}_{\mathrm{La_3I_9}} = \beta_T \cdot \left(\mathrm{TDF}_{\mathrm{LaI_3}} + \mathrm{TDF}_{\mathrm{La_2I_6}} \right),$$

$$\beta_T = \frac{\mathrm{TDF}_{\mathrm{Lu_3Cl_9}}}{\mathrm{TDF}_{\mathrm{LuCl_3}} + \mathrm{TDF}_{\mathrm{Lu_2Cl_6}}}, \quad \text{(A.1)}$$

where TDF means the thermodynamic functions $\Phi^\circ(T)$ or $H^\circ(T) - H^\circ(0)$.

A.5. $CeI_4^-{}_{,g}$. The thermodynamic functions of the $\mathrm{CeI_4^-}$ ions were computed in the RRHO approximation assuming a coincidence of the functions for $\mathrm{CeI_4^-}$ and $\mathrm{CeI_4}$ based on the molecular constants taken from [43] and the electronic states from [39].

A.6. $Ce_2I_7^-{}_{,g}$. The thermodynamic functions of $\mathrm{Ce_2I_7^-}$ ions were evaluated by a comparative method on the basis of those for $\mathrm{LnI_3}$, $\mathrm{LnI_4^-}$ (Ln = La, Ce) [22, 44], $\mathrm{Ce_2I_6}$ [40], and $\mathrm{La_2I_7^-}$ [14] using the following relation:

$$\mathrm{TDF}\left(\mathrm{Ce_2I_7^-}\right) = \beta_T' \cdot \mathrm{TDF}\left(\mathrm{Ce_2I_6}\right), \quad \text{(A.2)}$$

where

$$\beta_T' = \frac{\mathrm{TDF}\left(\mathrm{CeI_4^-}\right)/\mathrm{TDF}\left(\mathrm{CeI_3}\right)}{\mathrm{TDF}\left(\mathrm{LaI_4^-}\right)/\mathrm{TDF}\left(\mathrm{LaI_3}\right)} \cdot \frac{\mathrm{TDF}\left(\mathrm{La_2I_7^-}\right)}{\mathrm{TDF}\left(\mathrm{La_2I_6}\right)}. \quad \text{(A.3)}$$

The thermodynamic functions used in this work were approximated by the polynomial

$$\Phi^\circ(T) = a \ln x + b x^{-2} + c x^{-1} + d x + e x^2 + f x^3,$$
$$\left(x = \frac{T}{1000} \right). \quad \text{(A.4)}$$

The coefficients of (A.4) are listed in Table 10.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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