

Molecular and Ionic Sublimation of Neodymium Tribromide Polycrystals and Single Crystals

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Abstract—The molecular and ionic sublimation of polycrystals and single crystals under Knudsen effusion and Langmuir evaporation conditions is reported. In both sublimation regimes, the sublimation product at 780–1050 K contains neodymium tribromide monomer and dimer molecules, as well as the negative ions NdBr_4^- , Nd_2Br_7^- , and Br^- . The dimer-to-monomer flux ratio $j(\text{Nd}_2\text{Br}_6)/j(\text{NdBr}_3)$ is larger in the molecular beam coming out of the effusion hole, while the ratio of the sublimation fluxes of the negative ions, $j(\text{Nd}_2\text{Br}_7^-)/j(\text{NdBr}_4^-)$, is independent of the sublimation conditions. The partial pressures of the neutral components of the vapor have been determined, and the enthalpies and activation energies of sublimation of neodymium tribromide as monomer and dimer molecules and NdBr_4^- and Nd_2Br_7^- ions have been calculated. The equilibrium constants of ion–molecule reactions have been measured, and the enthalpies of these reactions have been determined. Based on these data, values of the thermodynamic properties $\Delta_f H^0(298.15)$ and $\Delta_f H^0(298.15)$ are recommended for the monomer and dimer molecules and the NdBr_4^- and Nd_2Br_7^- ions.

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This study of neodymium tribromide sublimation continues our systematic investigation of the molecular and ionic sublimation of lanthanide tribromide polycrystals under equilibrium conditions (Knudsen effusion) and lanthanide tribromide single crystals under conditions of free evaporation from an open surface (Langmuir evaporation) [1–5].

The saturation vapor pressure over NdBr_3 was measured earlier by the Knudsen effusion method [6, 7], boiling point method [8–10], torsion method [11], and mass spectrometry [12]. Gietmann et al. [12] detected dimers in the vapor phase, while the other authors [6–11] measured the total vapor pressure and processed the data under the assumption that the vapor consists only of monomers.

In this study, we calculate the second- and third-law enthalpies of sublimation of neodymium tribromide as monomers and dimers, using new experimental vapor pressure data, relevant data available from the literature, and an updated set of thermodynamic functions. Based on the results obtained, we recommend thermodynamic parameters of the monomer and dimer molecules.

In addition to performing thermodynamic experiments under Langmuir conditions, we studied the sublimation kinetics of an NdBr_3 single crystal for the first

time and, from the temperature dependences of ion currents, derived the activation energies of sublimation of NdBr_3 as monomers and dimers.

The ionic sublimation of neodymium tribromide was studied under both Knudsen effusion and Langmuir evaporation conditions. This study allowed the enthalpies of formation of the negatively charged ions NdBr_4^- and Nd_2Br_7^- to be determined for the first time.

EXPERIMENTAL

Mass spectrometric experiments were carried out on an MI 1201 commercial magnetic sector mass spectrometer ($\angle 90^\circ$, curvature radius of 200 mm) modified for high-temperature studies. The experimental setup and procedure are detailed elsewhere [1].

Neodymium tribromide (99.99%) was synthesized using the NH_4Br -based procedure [13, 14]. An NdBr_3 single crystal was grown by the vertical Bridgman technique using a neodymium tribromide powder sealed in a glass tube.

In the Knudsen measurements of sublimation, an NdBr_3 powder was evaporated from a molybdenum effusion cell. The ratio of the cross-sectional area of the cell to the effusion aperture area was about 400. In

Table 1. Electron impact ionization mass spectra of neodymium tribromide recorded using the effusion cell (EC) technique and sublimation from the open surface (OS) of a single crystal and the appearance energies (AE) of ions

	Technique	<i>T</i> , K	<i>E_e</i> , eV	Nd ⁺	NdBr ⁺	NdBr ₂ ⁺	NdBr ₃ ⁺	Nd ²⁺	NdBr ²⁺	NdBr ₂ ²⁺	Nd ₂ Br ₅ ⁺	Reference
Relative ion current, %	EC	858	70	23.9	12.3	100	11.8	4.3	2.0	0.1	1.1	[12]
		858	21	19.1	28.1	100	13.5	Not measured	Not measured	Not measured	0.6	
AE, eV	OS	858	70	14.8	7.7	100	12.3	The same	The same	The same	0.7	[12]
				18.1	13.5	10.3	10.2	31.6	27.0	Not measured	10.4	
				18.4	14.6	10.7	10.1	Not measured	Not measured	The same	11.3	

Note: The relative ion currents take into account the variety of isotopic species of the ions. The scale of ionizing electron energies is calibrated against the ionization energies of the silver atom and water molecule as standards. The error in the appearance energy of the ions is estimated at ± 0.5 eV.

Table 2. Coefficients of the equation $\log I = -A \times 10^3/T + B$

Ion	A	B	ΔT , K	N	A	B	ΔT , K	N
	effusion cell				open surface			
Nd ⁺	14.37 \pm 0.79	20.79 \pm 0.91	803–924	13	15.15 \pm 0.17	23.01 \pm 0.21	790–835	18
NdBr ⁺	14.85 \pm 0.87	21.06 \pm 1.01	802–924	12	15.11 \pm 0.44	22.69 \pm 0.55	802–825	9
NdBr ₂ ⁺	13.99 \pm 0.60	20.98 \pm 0.71	780–912	19	14.82 \pm 0.34	23.00 \pm 0.51	799–831	10
NdBr ₃ ⁺	14.87 \pm 0.87	21.06 \pm 0.99	803–924	12	15.12 \pm 0.13	22.90 \pm 0.16	799–879	17
Nd ²⁺	13.82 \pm 0.90	19.42 \pm 1.03	825–930	16				
NdBr ²⁺	13.64 \pm 0.93	19.08 \pm 1.05	861–910	7				
NdBr ₂ ²⁺	13.80 \pm 1.35	17.83 \pm 1.53	861–910	8				
Nd ₂ Br ₅ ⁺	19.43 \pm 2.06	25.36 \pm 2.33	851–930	19	20.04 \pm 0.12	27.38 \pm 0.14	814–880	15

Note: *N* is the number of measurements. The numbers after the sign \pm are standard deviations.

Langmuir measurements, an NdBr₃ single crystal was secured in a molybdenum holder. The (001) face of the crystal (3 \times 3 mm) was sublimed, which was obtained by cleavage immediately before mounting the evaporator in the mass spectrometer.

Molecular components of the vapor were identified while operating the ion source in the electron impact ionization mode. Mass spectra were recorded at an electron energy of $E_e = 70$ eV and a cathode emission current of $I_{emis} = 1$ mA. In ionic sublimation experiments, the thermal ions generated inside the effusion cell or on the crystal surface were extracted by a weak electric field of 10^4 – 10^5 V m⁻¹ produced between the cell and the collimator electrode.

RESULTS AND DISCUSSION

Molecular Sublimation

Mass spectra. The mass spectra obtained by electron impact ionization of a molecular beam (Table 1) in

the range 780–930 K were similar to the spectra of other LnBr₃ compounds [1–5] and indicated the presence of the Nd⁺, NdBr⁺, NdBr₂⁺, NdBr₃⁺, Nd₂Br₅⁺, Nd²⁺, NdBr²⁺, and NdBr₂²⁺ ions both in effusion measurements and in sublimation from an open single-crystal surface.

The standard procedure of assigning the observed ions to their molecular precursors, including an analysis of the shapes of the ionizations efficiency (IE) curves for various ions, measurement of the appearance energy (AE) of ions by linear extrapolation of the near-threshold portions of the IE curves (Table 1), and determination of the coefficients of the temperature dependences of ion currents ($\log I_i = -A \times 10^3/T + B$, Table 2), led us to the following conclusion: the ions containing one neodymium atoms result mainly from the ionization of the monomer molecule NdBr₃, and the Nd₂Br₅⁺ ion is a product of the dissociative ionization of the Nd₂Br₆ dimer.

Although the mass spectra obtained using the Knudsen and Langmuir sublimation techniques are qualitatively similar, they differ in their relative ion intensities. Figure 1 plots the temperature dependences of the relative partial ionization cross section Φ (ratio of the current due to a given ion to the total current due to all ions formed from a given molecule) for singly charged ions. Clearly, the Φ data obtained for various ions using the two sublimation techniques differ in magnitude and show somewhat different temperature dependences. This result once again demonstrates the distinctive features of electron impact fragmentation in the two sublimation techniques, confirming earlier observations for LuBr_3 [2] and HoBr_3 [4]. We explain these distinctive features at the qualitative level in terms of the “superthermal” vibrational–rotational excitation of the molecules being sublimed from the open surface of an ionic crystal. Specifically, we consider these features to arise from the conversion of the Stark energy of admolecules in the electric field of the excess surface charge of defect and impurity origins (see, e.g., [15–17]) into the vibrational–rotational excitation energy.

The partial pressures of molecules (p_i) in the vapor phase were calculated using the following standard relationship of electron impact ionization mass spectrometry:

$$p_i = kI_i T / \sigma_i^{mol}, \quad (1)$$

where k is the sensitivity constant of the instrument (determined by evaporation of silver metal in a separate experiment), T is the cell temperature, $I_i = \sum_j I_{ij} / (a_j \gamma_j)$

is the total current due to all types of ions forming from molecule i , a is the coefficient accounting for the natural abundances of the isotopes of ion j , γ is the ion-to-electron conversion efficiency (accepted to be $\gamma \sim M^{-1/2}$ [18], where M is the molecular weight of the ion), and σ_i^{mol} is the total ionization cross section of the i th molecule at the working energy of the ionizing electrons (calculated from the ionization cross sections of atoms (σ^{at}) [19] using the relationship $\sigma^{mol} = 0.75 \sum_j \sigma_j^{at}$ [20]).

The temperature dependences of the saturation vapor pressures (p , Pa) of monomer and dimer molecules were approximated by the equations

$$\log p(\text{NdBr}_3) = (-14.61 \pm 0.60) 10^3 / T + (15.39 \pm 0.71), \quad T = 780\text{--}924 \text{ K}; \quad (2)$$

$$\log p(\text{Nd}_2\text{Br}_6) = (-19.81 \pm 2.06) 10^3 / T + (18.75 \pm 2.33), \quad T = 851\text{--}930 \text{ K}. \quad (3)$$

Here, the numbers after the sign \pm are standard deviations.

Figure 2 plots the partial pressures of the components of the saturated vapor over neodymium tribro-

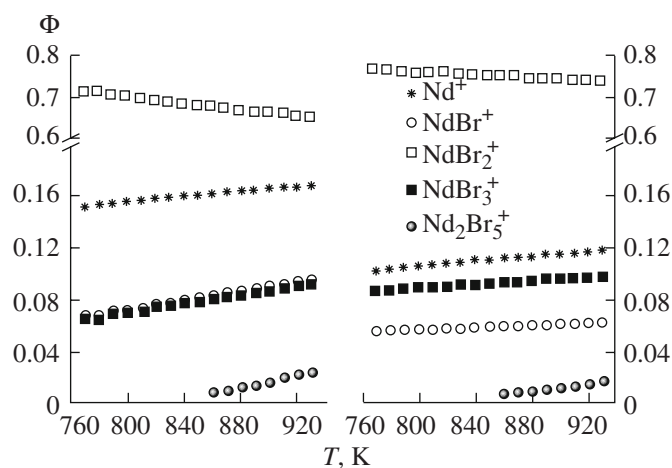


Fig. 1. Temperature dependences of the relative partial ionization cross sections (Φ) of the NdBr_3 molecule under electron impact in the Knudsen and Langmuir sublimation techniques.

mid according to our data, mass spectrometric data reported by Gietmann et al. [12], and total vapor pressure data [6–11]. Clearly, the scatter in the vapor pressure data for NdBr_3 is greater than one order of magnitude. Our data fall in the middle of the range of the pressures determined by total vapor pressure measurements [6, 7, 11] by the effusion method [6, 7] and the torsion method [11] and exceed the mass spectrometric pressure values reported in [12] by a factor of about 4. The proportion of dimer molecules in the temperature range examined is at most 1%, being 0.07% at 700 K, 0.3% at 800 K, and 0.9% at 900 K.

The enthalpy of sublimation of NdBr_3 as monomer and dimer molecules were derived from the temperature dependences of the partial pressures of the components of the saturated vapor (Table 3) using the second- and third-law data processing techniques. The necessary thermodynamic functions of NdBr_3 in the condensed state were calculated by G.A. Bergman (Joint Institute for High Temperatures, Russian Academy of Sciences) [21]. The thermodynamic functions of gaseous NdBr_3 were calculated by us in the rigid rotor–harmonic oscillator (RRHO) approximation. In these calculations, we used the molecular constants recommended based on an analysis of available experimental and theoretical data [22]. The thermodynamic functions of the dimer Nd_2Br_6 were estimated by a comparative method, as in the case of Lu_2Br_6 [2], under the assumption that the ratio of a thermodynamic function of the monomer to the same function of the dimer (derived from molecular parameters taken from [23, 24]) is invariable throughout the lanthanide series and is equal to the same ratio averaged between lanthanum and dysprosium.

The results of the processing of the totality of experimental data using a single set of thermodynamic func-

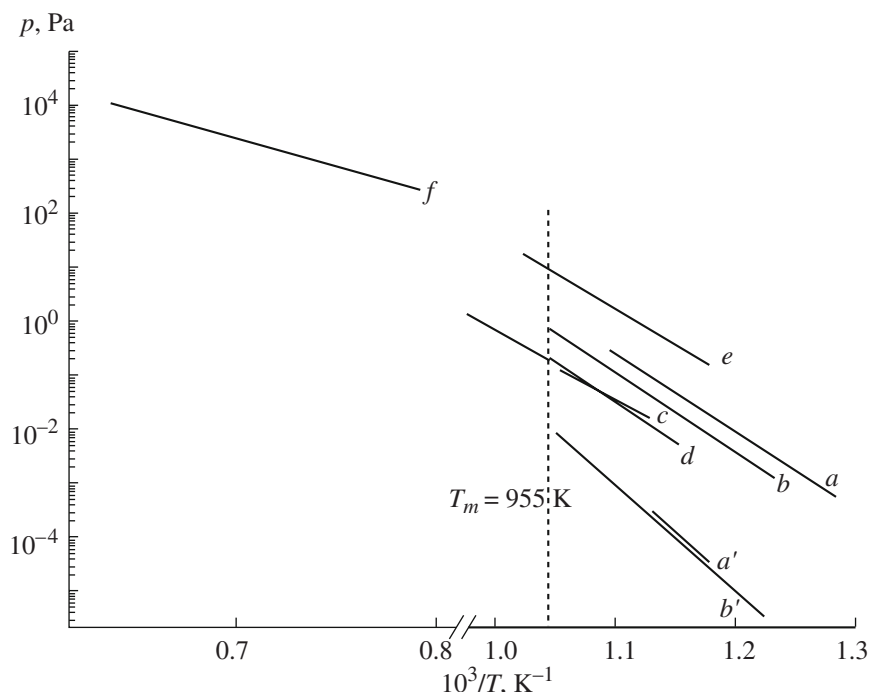


Fig. 2. Temperature dependences of the vapor pressure over neodymium tribromide: (a) monomer, this work; (a') dimer, this work; (b) monomer [12]; (b') dimer [12]; (c) [7]; (d) [11]; (e) [6]; (f) [8–10].

tions (Table 4) are presented in Table 5. In the calculation of the enthalpy of sublimation as monomers, the total pressure data [7–11] were corrected for the vapor composition derived from mass spectrometric data. It can be seen from Table 5 that the enthalpies of sublimation/evaporation as monomer molecules calculated by two independent methods from data of different authors fall between 262.1 and 317.2 kJ mol⁻¹ (second law) or between 274.7 and 305.9 kJ mol⁻¹ (third law). A more detailed data analysis based on examination of the temperature variation of the third-law enthalpy of sublimation ($\Delta_s H^\circ(298.15)$) and on a comparison between experimental (second-law) and theoretically calculated (third-law) entropies of sublimation ($\Delta_s S^\circ(T)$) did not indicate that the data of some particular study are preferable. For this reason, we accepted the weighted average value of $\Delta_s H^\circ(298.15) = 298 \pm 5$ kJ mol⁻¹ as the recommended enthalpy of sublimation. This value was calculated using the formula

$$\Delta_s H^\circ(298.15) = \sum_i k_i \Delta_s H_i^\circ(298.15), \quad (4)$$

where $k_i = 0.5/(a_i / \sum_i a_i) + 0.5/(b_i / \sum_i b_i)$,

$$a_i = \sqrt{\sum_i \left(\frac{d}{dT} \Delta_s H_i^\circ(298.15)^{\text{III}} \right)^2},$$

$$b_i = \sqrt{\sum_i \left(\Delta_s S_i^\circ(T)^{\text{II}} - \Delta_s S_i^\circ(T)^{\text{III}} \right)^2},$$

$\Delta_s H^\circ(298.15)^{\text{III}}$ is the third-law enthalpy of sublimation, $\Delta_s S^\circ(T)^{\text{II}}$ is the second-law entropy of sublimation, and $\Delta_s S^\circ(T)^{\text{III}}$ is the third-law entropy of sublimation.

The second- and third-law enthalpies of sublimation of neodymium tribromide as dimer molecules (Table 5) are in good agreement with one another and with the enthalpy data reported in [12]. The value of $\Delta_s H^\circ(298.15) = 398 \pm 20$ kJ mol⁻¹ was accepted as the recommended value.

The enthalpies of formation ($\Delta_f H^\circ(298.15)$) of the monomer (-566 ± 6 kJ mol⁻¹) and dimer (-1333 ± 20 kJ mol⁻¹) were obtained by combining the accepted values of the enthalpies of sublimation and the enthalpy of formation of crystalline neodymium tribromide [25]: $\Delta_f H^\circ(\text{NdBr}_3, \text{cr}, 298.15) = -864.0 \pm 3.0$ kJ mol⁻¹. The value that we obtained for the NdBr₃ molecule (-566 ± 6 kJ mol⁻¹) differs markedly from the enthalpy estimated within the valence state atoms in molecules model [26].

The activation energies of sublimation (E_s) of crystalline neodymium tribromide as monomer and dimer molecules were derived from the regression coefficients of the relationships between $\log(\sum_j I_j T / (a_j \gamma_j))$ and $1/T$ (j : Nd⁺, NdBr⁺, NdBr₂⁺, NdBr₃⁺, Nd²⁺, NdBr²⁺, NdBr₂²⁺) and between $\log I_{\text{Nd}_2\text{Br}_3^+} T$ and $1/T$ observed under free sublimation conditions: $E_s(\text{NdBr}_3, 820 \text{ K}) = 292.1 \pm 3.3$ kJ mol⁻¹ and

Table 3. Experimental equilibrium constants of the sublimation reactions of the neodymium tribromide monomer ($K^0 = p_{\text{mon}}/p^0$, $p^0 = 101325 \text{ Pa}$) and dimer ($K^0 = p_{\text{dim}}/p^0$) and the enthalpies of ion–molecule reactions

$T, \text{ K}; \ln K^0$					
$\text{NdBr}_{3, \text{cr}} = \text{NdBr}_{3, \text{g}}$					
886, -14.044;	874, -14.855;	859, -15.542;	851, -15.844;	827, -16.878;	803, -18.304;
780, -19.492;	876, -14.821;	861, -14.845;	877, -14.217;	912, -13.183;	883, -14.074;
866, -14.652;	839, -15.866;	824, -16.454;	803, -17.478;	904, -13.141;	876, -14.305;
832, -15.527.					
$2\text{NdBr}_{3, \text{cr}} = \text{Nd}_2\text{Br}_{6, \text{g}}$					
868, -20.529;	889, -19.709;	906, -19.087;	930, -16.492;	906, -18.487;	923, -16.923;
873, -20.071;	875, -20.164;	903, -18.929;	904, -18.599;	886, -19.748;	876, -20.513;
859, -21.330;	851, -21.810;	865, -20.301;	875, -20.647;	861, -20.738;	877, -20.149;
884, -20.018.					
$\text{NdBr}_3 + \text{LuBr}_4^- = \text{LuBr}_3 + \text{NdBr}_4^-$					
947, -1.245;	971, -1.802;	969, -1.880;	912, -1.339;	913, -1.777;	881, -1.554;
899, -1.862;	887, -1.313;	911, -1.376;	935, -1.923;	852, -2.450;	905, -1.803;
940, -1.515;	907, -2.237.	881, -1.606.			
$\text{Nd}_2\text{Br}_7^- = \text{NdBr}_{3, \text{cr}} + \text{NdBr}_4^-$					
953, -3.428;	1028, -3.450;	1043, -3.260;	1053, -3.750;	1053, -4.049;	896, -2.014;
923, -2.281;	896, -2.078;	870, -2.224;	889, -2.119;	920, -2.204;	950, -2.669.

Table 4. Thermodynamic functions (I) $\Phi^0(T)$ ($\text{J mol}^{-1} \text{ K}^{-1}$) and (II) $H^0(T) - H^0(0)$ (J mol^{-1}) used in the calculations

$T, \text{ K}$	$\text{NdBr}_{3, \text{cr}}$		NdBr_3		Nd_2Br_6		NdBr_4^-		Nd_2Br_7^-	
	I	II	I	II	I	II	I	II	I	II
298.15	108.74	25.30	341.37	20.57	525.91	44.81	372.32	26.77	549.75	51.57
700	184.19	65.77	403.78	53.54	663.38	117.46	453.60	69.73	704.30	135.22
800	196.88	76.97	414.05	61.81	686.03	135.67	466.97	80.49	729.87	156.17
900	208.34	88.50	423.19	70.09	706.20	153.90	478.87	91.27	752.65	177.14
1000	220.99	147.55	431.42	78.38	724.36	172.14	489.59	102.05	773.20	198.13

Note: The errors in the Gibbs energy functions were estimated as was suggested in [20] and were taken to be $\pm 12 \text{ J mol}^{-1} \text{ K}^{-1}$ for LnBr_3 and $\pm 40 \text{ J mol}^{-1} \text{ K}^{-1}$ for Ln_2Br_6 ($T = 1000 \text{ K}$).

Table 5. Enthalpies (kJ mol^{-1}) and entropies ($\text{J mol}^{-1} \text{K}^{-1}$) of sublimation of NdBr_3 as monomer and dimer molecules (N is the number of measurements, and T_{hm} is the harmonic mean temperature)

ΔT , K	N	T_{hm}	Second law			Third law		Reference
			$\Delta_s H^0(T_{\text{hm}})$	$\Delta_s S^0(T_{\text{hm}})$	$\Delta_s H^0(298.15)$	$\Delta_s H^0(298.15)$	$\Delta_s S^0(T_{\text{hm}})$	
$\text{NdBr}_3, \text{cr} = \text{NdBr}_3, \text{g}$								
780–912	19	853	279.6 ± 11.5	198.9 ± 13.5	291.7 ± 11.9	289.4 ± 12.0	196.1 ± 12.0	This work
812–954	65	884	287.4 ± 3.8	200.7 ± 4.0	300.5 ± 3.8	295.5 ± 12.0	195.1 ± 12.0	[12]
849–975		912	251.3 ± 3.8	183.4 ± 3.9	274.7 ± 3.8	274.7 ± 12.0	194.2 ± 12.0	[8]
889–948	6	918	247.7 ± 3.8	146.3 ± 3.9	262.1 ± 3.8	305.9 ± 12.0	193.7 ± 12.0	[7]
866–954		910	289.4 ± 2.9	193.0 ± 3.8	303.5 ± 2.9	304.5 ± 12.0	194.1 ± 12.0	[11]
956–1019		987	253.6 ± 5.7	154.2 ± 5.7	317.2 ± 5.7	305.6 ± 12.0	142.2 ± 12.0	[11]
1258–1559		1409	199.0	107.3	292.9	303.6 ± 12.0	116.7 ± 12.0	[8–10]
$2\text{NdBr}_3, \text{cr} = \text{Nd}_2\text{Br}_6, \text{g}$								
851–930	19	884	379.3 ± 39.4	263.1 ± 39.6	395.8 ± 39.6	397.2 ± 30.0	264.7 ± 30.0	This work
817–951	65	884	379.5 ± 8.1	261.7 ± 7.7	396.0 ± 8.1	398.6 ± 30.0	264.8 ± 30.0	[12]

Note: For the second-law values, the numbers after the sign \pm are standard deviations. For the third-law values, these numbers are the limiting errors taking into account the statistical error and the systematic errors in the temperature and pressure measurements and in the reduced Gibbs energy function.

$E_s(\text{Nd}_2\text{Br}_6, 838 \text{ K}) = 383.6 \pm 7.0 \text{ kJ mol}^{-1}$). These values are equal to the enthalpies of sublimation of the monomer and dimer molecules within the indicated errors. At the same time, the dimer-to-monomer flux ratio is much larger in the beam coming out of the effusion hole. For example, at 850 K, the flux ratio $j(\text{Nd}_2\text{Br}_6)/j(\text{NdBr}_3)$ for the NdBr_3 surface under the Knudsen and Langmuir conditions is 1.71×10^{-3} and 5.31×10^{-6} , respectively; that is, the fraction of sublimed dimers decreases by more than 2 orders of magnitude on passing from the dynamic equilibrium sublimation conditions to sublimation from an open surface. This factor provides an estimate for the ratio of the sublimation coefficients of the dimer $\alpha_s(\text{Nd}_2\text{Br}_6)$ and monomer $\alpha_s(\text{NdBr}_3)$ under the Langmuir conditions.

Ionic Sublimation

Mass spectra. Here, we present the first study of ion sublimation from the NdBr_3 surface between 800 and 1050 K. Both in equilibrium sublimation and in free sublimation, we observed the thermal emission of the negative ions NdBr_4^- and Nd_2Br_7^- . In the free sublimation of an NdBr_3 single crystal, we observed a weak signal from the bromide ion. The ion current ratio $I(\text{NdBr}_4^-)/I(\text{Nd}_2\text{Br}_7^-)$ in the temperature range examined varied within 1–2 orders of magnitude and was independent of the sublimation conditions. A similar result was obtained in earlier studies [1, 2, 4]. This corrob-

*The positive ion mass spectra always indicated intensive emission of ions of alkali metals, which were present in the sample as an impurity.

orates the hypothesis that the sublimation of ionic clusters takes place via a "diffusionless" mechanism [2].

The enthalpy and activation energy of sublimation of the NdBr_4^- ion were derived from the slope of the $\log \log IT^{1/2} = f(1/T)$ curve. At the mean experimental temperature, $\Delta_s H^\circ(\text{NdBr}_4^-, 879 \text{ K}) = 290.0 \pm 13.6 \text{ kJ mol}^{-1}$ and $E_s(\text{NdBr}_4^-, 848 \text{ K}) = 286.5 \pm 13.5 \text{ kJ mol}^{-1}$. Within the indicated errors, these values are equal to the enthalpy of sublimation ($279.6 \text{ kJ mol}^{-1}$) and the activation energy of sublimation ($292.1 \text{ kJ mol}^{-1}$) of the NdBr_3 monomer.

The enthalpies of formation of ions. The enthalpy of formation of the NdBr_4^- ion was determined by a procedure based on investigation of gas-phase ion-molecule exchange reactions in binary or more complex systems [27]. To make use of this procedure, we studied the $\text{LuBr}_3\text{-NdBr}_3$ system and measured the equilibrium constant of the following reaction (Table 3):



In this reaction, the LuBr_4^- ion serves as a standard. Its enthalpy of formation, $\Delta_f H^\circ(\text{LuBr}_4^-, \text{g}, 298.15 \text{ K}) = -1085 \pm 23 \text{ kJ mol}^{-1}$, was reliably determined in our earlier study [2]. The second- and third-law calculations of the enthalpy of reaction (5), $\Delta_r H^\circ(298.15 \text{ K})$, led to similar values of 20 ± 20 and $18.6 \pm 5.0 \text{ kJ mol}^{-1}$, respectively. Combining the latter with the enthalpy of formation of crystalline NdBr_3 [25] yielded $\Delta_f H^\circ(\text{NdBr}_4^-, \text{g}, 298.15 \text{ K}) = -1094 \pm 27 \text{ kJ mol}^{-1}$.

For calculating the enthalpy of formation of the Nd_2Br_7^- ion, we measured the equilibrium constant and enthalpy of the heterophase reaction



in the sublimation of pure neodymium tribromide (Table 3).

The third-law enthalpy of reaction (6) is $\Delta_r H^\circ(298.15 \text{ K}) = -82.8 \pm 44 \text{ kJ mol}^{-1}$. The corresponding enthalpy of formation of the Nd_2Br_7^- ion is $\Delta_f H^\circ(298.15 \text{ K}) = -1875 \pm 44 \text{ kJ mol}^{-1}$.

The thermodynamic functions of NdBr_4^- and Nd_2Br_7^- necessary for calculating the enthalpies of formation of these ions (Table 4) were calculated in the RRHO approximation. The molecular parameters for the NdBr_4^- ion were estimated through ab initio calculations of the structure, force fields, and vibrational spectra of the LaBr_4^- and LuBr_4^- ions [28] under the assumption that the molecular constants of LnX_4^- in the

lanthanide series are linearly independent. The thermodynamic functions of Nd_2Br_7^- were estimated by an additivity method using an empirical correction, as was done in [29]. The thermodynamic functions of the LuBr_3 molecule and the LuBr_4^- ion were taken from [2]; those of crystalline NdBr_3 , from [21]. The following enthalpies of formation ($\Delta_f H^\circ(298.15 \text{ K})$, kJ mol^{-1}) were also used: LuBr_3 , -538 ± 15 [2]; LuBr_4^- , -1085 ± 23 [2]; NdBr_3 , cr, -864.0 ± 3.0 [25].

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