

CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

A Mass Spectrometric Study of the Sublimation of Lutetium Tribromide under Knudsen and Langmuir Conditions

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Abstract—The molecular and ionic sublimation of lutetium tribromide under thermodynamic equilibrium (Knudsen effusion) conditions and from the open surface of a LuBr₃ single crystal (Langmuir conditions) was studied by high-temperature mass spectrometry. Vapor contained the LuBr₃, Lu₂Br₆, Lu₃Br₉, and Lu₄Br₁₂ molecules and the Br[−], LuBr₄[−], Lu₂Br₇[−], and Lu₃Br₁₀[−] negative ions. The partial pressures of the molecules in saturated vapor and the ratio between the sublimation coefficients of monomers and dimers under free vaporization conditions were determined. The degree of the electron impact-induced fragmentation of LuBr₃ molecules under Knudsen and Langmuir sublimation conditions was analyzed. The second and third laws of thermodynamics were used to calculate the enthalpies of sublimation in the form of monomers and oligomers (Knudsen vaporization) and the corresponding activation energies of sublimation (Langmuir vaporization). Ion–molecular equilibria with the participation of negative ions were studied. The enthalpies of formation of molecules and ions in the gas phase were obtained.

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INTRODUCTION

The determination of the thermodynamic, structural, and spectral characteristics of lanthanide halides is a complex research problem of high-temperature chemistry, which has been the focus of interest of a large number of research teams (e.g., see reviews [1–3]). Apart from fundamental studies, these data are of interest for technologies in metallurgy and power engineering [4]. In particular, data on lanthanide trihalide vapor pressure and composition are used for growing pure and doped LnX₃ crystals, which are extensively used in optical [5] and scintillation [6] devices and for creating energy-saving light sources (metal-halide lamps) [7].

This work continues our systematic studies of the molecular and ionic sublimation of lanthanide tribromides under equilibrium conditions (with the use of the Knudsen effusion method) and in free vaporization from the open surface of a LnBr₃ single crystal (Langmuir conditions) [8] for the example of lutetium tribromide.

Saturated vapor pressure over LuBr₃ was measured in [9] and [10], where the boiling point and torsional-effusion integral methods, respectively, were used. The earliest data on the molecular composition of saturated vapor over lutetium tribromide were obtained in [11,

12]; mono-, di-, and trimeric molecules were observed in the mass spectrum of LuBr₃. Unfortunately, neither absolute component vapor pressures, nor thermodynamic function values used in calculations of the enthalpies of sublimation were reported in these works. We cannot therefore estimate the reliability of the data obtained in [11, 12]. The kinetics of sublimation and the ionic composition of vapor over LuBr₃ have not been studied.

The purpose of this work was to (1) determine the fraction of oligomer molecules in the vapor phase under equilibrium sublimation (the Knudsen method) and free vaporization (the Langmuir method) conditions, (2) refine the enthalpy of sublimation of LuBr₃ in the form of monomers and determine the enthalpy of sublimation in the form of oligomers using a new unified set of thermodynamic functions for the condensed and gaseous states and obtain the thermodynamic characteristics of molecules in the gas phase, (3) determine the activation energies of sublimation, (4) analyze the rules that governed fragmentation in the electron-induced ionization of molecular beams from an effusion cell and the open surface of a single crystal, and (5) analyze the composition of and ratio between charged vapor components in two sublimation regimes and determine the thermodynamic characteristics of ions. The novelty of the approach suggested is a complex

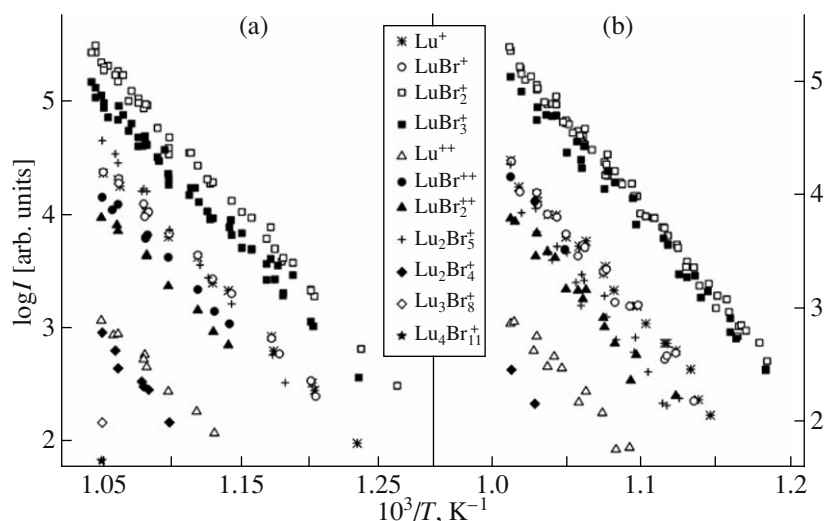


Fig. 1. Temperature dependences of ion currents I in electron-impact mass spectra measured under (a) Knudsen and (b) Langmuir conditions.

study of the thermodynamic and kinetic characteristics of the sublimation of LuBr_3 accompanied by an analysis of both molecular and ionic vapor components.

EXPERIMENTAL

We used an MI 1201 ($\angle 90^\circ$, radius of curvature 200 mm) commercial magnetic mass spectrometer modified for high-temperature measurements. The procedures for measurements and compound synthesis are described in detail in [8].

Sublimation under Knudsen conditions was studied for a LuBr_3 powder of 99.999% purity. The substance was vaporized from a molybdenum effusion cell with a ratio of ~ 400 between the cell cross section and effusion orifice (0.6 mm in diameter) areas. The substance was loaded into the cell from evacuated ampules at atmospheric pressure. To remove adsorbed moisture, the cell with the substance was dehydrated in a $\sim 10^{-1}$ Pa vacuum directly in the mass spectrometer at $\sim 150^\circ\text{C}$ for several hours. Sublimation under Langmuir conditions was studied using a $3 \times 3 \times 10$ mm LuBr_3 single crystal mounted in a cylindrical holder made of molybdenum. The (001) crystal face (3×3 mm) cleaved directly before installing the vaporizer into the mass spectrometer was exposed to sublimation.

The molecular vapor components were analyzed when the ion source operated under electron impact conditions. The mass spectra were measured at ionizing electron energy $E_e = 70$ eV and emission current from the cathode $I_e = 1$ mA. In ionic sublimation experiments, ions of the thermal origin formed inside the effusion cell or on the surface of the crystal were drawn out by a low electric field (10^4 – 10^5 V/m) created between the cell and a collimating electrode.

RESULTS AND DISCUSSION

Mass Spectra. The qualitative composition of single- and double-charged ions with one lutetium atom (Lu^+ , LuBr^+ , LuBr_2^+ , LuBr_3^+ , Lu^{2+} , LuBr^{2+} , and LuBr_2^{2+}) was the same in electron-impact mass spectra obtained under effusion conditions and under the conditions of sublimation from an open single crystal surface. In addition to the ions specified above, more complex ions, such as Lu_2Br_5^+ , Lu_2Br_4^+ , Lu_3Br_8^+ , and $\text{Lu}_4\text{Br}_{11}^+$, were recorded under Knudsen conditions, whereas only Lu_2Br_5^+ and Lu_2Br_4^+ were observed for Langmuir vaporization. The temperature dependences of corrected ion currents $I = I_j/a_j\gamma_j$ (the index j denotes the isotope measured, a is the coefficient of the natural abundance of this isotope, and γ is the ion-electron conversion coefficient; $\gamma \sim M^{-1/2}$ [13], where M is the molecular weight of the ion) are shown in Fig. 1. The coefficients of the linear approximation equation

$$\log I = -A \times 10^3/T + B \quad (1)$$

are listed in Table 2. This table also contains the appearance energies AE of ions obtained by the linear extrapolation of the near-threshold ionization efficiency curve regions. The energy scale of ionizing electrons was calibrated using Ag and H_2O as references.

An analysis of the coefficients of (1), AE values, and the shapes of the ionization efficiency curves, which did not contain pronounced kinks, led us to conclude that the Lu^+ , LuBr^+ , LuBr_2^+ , LuBr_3^+ , Lu^{2+} , LuBr^{2+} , and LuBr_2^{2+} ions were largely formed from monomeric LuBr_3 molecules with negligibly small possible contri-

Table 1. Electron impact mass spectra for sublimation under Knudsen and Langmuir conditions and ion appearance energies (AE)

Value	Conditions	T , K	E_e , eV	Lu^+	LuBr^+	LuBr_2^+	LuBr_3^+	Lu^{2+}	LuBr^{2+}	LuBr_2^{2+}	Lu_2Br_5^+	Lu_2Br_4^+	Lu_3Br_8^+	$\text{Lu}_4\text{Br}_{11}^+$
I , %	Knudsen	947	70	12	12	100	48	0.5	7	5	20	0.4	0.1	~ 0.05
		947 [11]	35	37	29	100	37				3.6	1.1	0.13	
		1061 [12]	50	37	35	100	21				12			
		1061	70	10	10	100	45	0.4	5	4	36	0.5		
	Langmuir	953	70	10	10	100	54	1	8	3	7			
AE , eV				21.9	16.1	12.0	10.8				10.7			

Note: Ion currents are given taking into account ion isotope varieties and ion-electron conversion coefficients (see text); the error in appearance energies was estimated at ± 0.5 eV; the second *I* values at 1061 K were obtained by extrapolation according to (1).

Table 2. Coefficients of Eq. (1), *N* is the number of measurements

Ion	<i>A</i>	<i>B</i>	ΔT , K	<i>N</i>	<i>A</i>	<i>B</i>	ΔT , K	<i>N</i>
	Knudsen conditions				Langmuir conditions			
Lu ⁺	12.78 \pm 0.22	17.86 \pm 0.25	810–952	15	15.38 \pm 0.37	19.84 \pm 0.40	873–988	22
LuBr ⁺	12.68 \pm 0.26	17.77 \pm 0.29	830–952	14	15.67 \pm 0.53	20.12 \pm 0.56	881–988	19
LuBr ₂ ⁺	13.45 \pm 0.11	19.49 \pm 0.12	791–953	43	15.47 \pm 0.13	20.90 \pm 0.15	845–989	68
LuBr ₃ ⁺	13.19 \pm 0.19	18.90 \pm 0.21	809–953	49	14.82 \pm 0.32	20.06 \pm 0.34	845–988	28
Lu ²⁺	12.05 \pm 0.50	15.74 \pm 0.54	884–953	9	14.57 \pm 0.94	17.67 \pm 0.98	916–988	12
LuBr ₂ ²⁺	12.26 \pm 0.37	17.06 \pm 0.40	876–953	10				
LuBr ₂ ²⁺	12.59 \pm 0.38	17.24 \pm 0.41	876–953	9	15.21 \pm 0.78	19.22 \pm 0.83	891–988	16
Lu ₂ Br ₅ ⁺	15.74 \pm 0.24	21.20 \pm 0.26	846–953	12	17.47 \pm 0.78	21.74 \pm 0.83	889–988	21
Lu ₂ Br ₄ ⁺	14.92 \pm 1.38	18.61 \pm 1.48	910–953	7				

butions of oligomer fragmentation. The Lu₂Br₅⁺ and Lu₂Br₄⁺ ions were formed in the ionization of Lu₂Br₆ dimeric molecules, and the Lu₃Br₈⁺ and Lu₄Br₁₁⁺ ions, from Lu₃Br₉ trimers and Lu₄Br₁₂ tetramers.

The mass spectra obtained in this work at 947 and 1061 K are compared in Table 1 with the results of earlier studies [11, 12]. As distinct from [11, 12], we observed double-charged Lu²⁺, LuBr₂²⁺, and LuBr₂²⁺ ions, whose contribution to the total ion current was ~6%. A substantially lower relative current of Lu₂Br₅⁺ ions reported in [11, 12] is also noteworthy. In other words, in those works, the fraction of dimers in vapor was strongly underestimated compared with the results of the present study. As concerns [12], this can be a consequence of the use of a comparatively long effusion nozzle (~1 mm at a diffusion orifice diameter of 0.6 mm) and a monopole mass analyzer with pronounced mass

discrimination. The reason for discrepancies between this work and [11], where an MI 1201 mass spectrometer similar to ours was used, is unclear.

The thermodynamic characteristics of sublimation. The partial pressures of molecules in vapor were calculated according to the standard mass spectrometric procedure with electron impact-induced ionization by the equation

$$p_i = kTI_i/\sigma_i^{\text{mol}}, \quad (2)$$

where *k* is the sensitivity constant of the instrument (determined in a separate experiment with vaporization of silver), *T* is the temperature of the cell, σ_i^{mol} is the total ionization cross section of the *i*th molecule at the working energy of ionizing electrons (calculated from the ionization cross sections of atoms σ^{at} [14] by the equation $\sigma^{\text{mol}} = 0.75 \sum_j \sigma_j^{\text{at}}$ [15]), and *I_i* is the total ion current of ions of all types formed from the *i*th molecule.

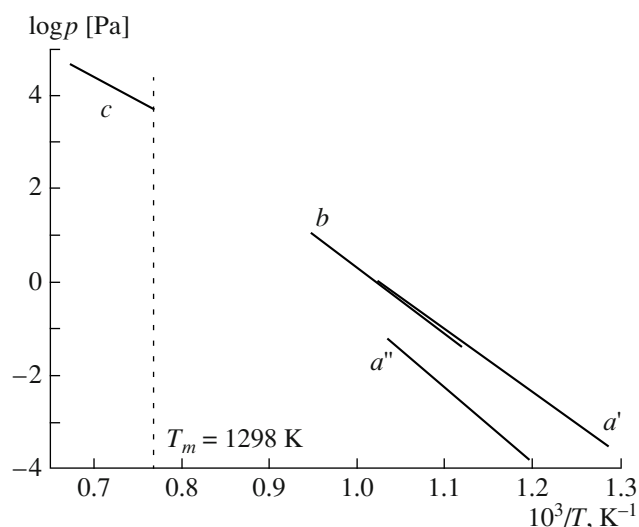


Fig. 2. Temperature dependences of saturated vapor pressures over LuBr_3 : (a') our data (monomers), (a'') our data (dimers), (b) data from [10], and (c) data from [9] (b and c are total vapor pressures).

The temperature dependences of saturated vapor pressures p (Pa) of monomeric and dimeric molecules were approximated by the equations

$$\log p(\text{LuBr}_3) = (-13.569 \pm 0.107) \times 10^3/T + (13.900 \pm 0.121), \quad 791\text{--}953 \text{ K}, \quad (3)$$

$$\log p(\text{Lu}_2\text{Br}_6) = (-16.112 \pm 0.235) \times 10^3/T + (15.444 \pm 0.260), \quad 846\text{--}953 \text{ K}. \quad (4)$$

The values preceded by \pm are the standard deviations.

The partial saturated vapor pressures over lutetium tribromide are shown in Fig. 2 together with the total vapor pressure [9, 10]. We see that the experimental data obtained over a fairly wide temperature range well correspond to each other. The mole fraction of dimeric molecules changes from 2 to 7% over the temperature range studied, and the mole fractions of tri- and tetramers (not shown in Fig. 2) do not exceed ~ 0.03 and $\sim 0.01\%$, respectively.

The enthalpies of sublimation of lutetium tribromide in the form of monomeric and dimeric molecules were found from the temperature dependences of the partial pressures of saturated vapor components using the procedure for experimental data processing according to the second and third laws of thermodynamics. The thermodynamic functions of LuBr_3 in the condensed state necessary for these calculations were obtained by Bergman (Joint Institute of High Temperatures, Russian Academy of Sciences) [16]. The thermodynamic functions of LuBr_3 in the gas state were calculated in the rigid rotator-harmonic oscillator approximation. We used the molecular constants recommended in [1] on the basis of an analysis of the experimental and theoretical data available. The functions for Lu_2Br_6

dimeric molecules were estimated by the comparative method from the averaged ratio between the functions of lanthanum and dysprosium tribromide monomers and dimers¹ calculated from the Kovács molecular parameters [17]; we assumed that this ratio was constant over the lanthanide series. The temperature dependence of the reduced Gibbs energy function $\Phi^\circ(T) = -[G^\circ(T) - H^\circ(0)]/T$ that we used was approximated by the polynomial [15]

$$\Phi^\circ(T), \text{ J/(mol K)} = a + b \ln x + c \times 10^{-3} x^{-2} + dx^{-1} + ex + fx^2 + gx^3 \quad (x = T \times 10^{-4}). \quad (5)$$

The coefficients of this polynomial are listed in Table 3.

The results obtained in processing the whole set of the experimental data on saturated vapor pressure, including the literature data, according to the second and third laws of thermodynamics on the basis of the unified set of thermodynamic functions are listed in Table 4. The original data from [9, 10], where the total vapor pressure was determined, were corrected for the partial pressures of monomeric molecules taking into account vapor composition on the basis of the $p(\text{LuBr}_3)/p(\text{Lu}_2\text{Br}_6)$ ratio obtained in this study. The results reported in [9] (vapor pressures over liquid LuBr_3) were recalculated by the extrapolation of the $p(\text{LuBr}_3)/p(\text{Lu}_2\text{Br}_6)$ values to the temperature above the melting point ($T_m = 1298 \text{ K}$) taking into account the enthalpy of fusion $\Delta_m H^\circ(\text{LuBr}_3) = 60 \text{ kJ/mol}$ [16].

According to Table 4, the enthalpies of sublimation in the form of monomeric molecules calculated using the second and third laws of thermodynamics from the vapor pressure data obtained by various authors agree with each other quite satisfactorily. A more detailed analysis of the results was based on the examination of the temperature-induced changes in the enthalpies of sublimation calculated by the third law and a comparison of the entropies of sublimation determined experimentally and calculated by the third law. The results of this analysis are shown in Fig. 3. We see that they are evidence of a high reliability of the results obtained in this work. Indeed, the $\Delta_s H^\circ(298.15)$ value varies insignificantly as the temperature increases, and the difference between the experimental and calculated entropies of sublimation is very small.

Note that the refinement of the results obtained in [9, 10] by taking into account the fraction of dimeric molecules in vapor improves the consistency of the whole set of the enthalpies of sublimation. For dimeric molecules, the enthalpies and entropies of sublimation calculated by the second and third laws satisfactorily agree with each other. Formally, our enthalpies of sublimation closely agree with the data obtained in [11]. However, unfortunately, [11] contains neither the experimental vapor pressure data themselves nor the thermodynamic functions used to calculate them (or initial

¹ The difference in the ratio between the Φ° potentials was $\sim 1\%$ over a wide temperature range.

Table 3. Parameters of polynomial (5)

Compound	<i>a</i>	<i>b</i>	<i>−c</i>	<i>d</i>	<i>e</i>	<i>−f</i>	<i>g</i>
LuBr ₃	582.384	81.5300	0.922285	0.473940	20.7695	60.5469	85.9942
Lu ₂ Br ₆	1066.06	177.07	1.91511	1.08499	52.8546	145.212	201.253
LuBr ₄ [−]	698.285	106.566	1.10030	0.637100	19.8434	58.6576	84.4993
Lu ₂ Br ₇ [−]	1165.24	200.040	2.25532	1.28785	77.2338	204.541	279.748

Table 4. Enthalpies (kJ/mol) and entropies (J/(mol K)) of sublimation of LuBr₃ in the form of monomers and dimers and enthalpies of ion-molecular reactions (*T*_{mh} is the mean harmonic temperature)

ΔT , K	N	T_{mh}	Second law			Third law	Refs.
			$\Delta_{\text{s}}H^{\circ}(T_{\text{mh}})$	$\Delta_{\text{s}}S^{\circ}(T_{\text{mh}})$	$\Delta_{\text{s}}H^{\circ}(298.15)$	$\Delta_{\text{s}}H^{\circ}(298.15)$	
LuBr ₃ (cr) = LuBr ₃							
791–953	43	884	259.8 ± 2.0	170.4 ± 2.0	273.6 ± 2.0	275.9 ± 12.0	This work
903–1038	110	966	268.8 ± 9.0	178.8 ± 9.0	285.2 ± 9.0	276.8 ± 12.0	[10]
1305–1468		1382	265.1 ± 9.0	174.0 ± 9.0	281.5 ± 9.0	277.5 ± 12.0	[10]
			187.8 ± 11.0	119.5 ± 11.0	280.8 ± 11.0	267.5 ± 12.0	[9]
			171.2 ± 11.0	103.9 ± 11.0	264.2 ± 11.0	272.4 ± 12.0	[9]
794–1073		907	260 ± 2		274 ± 3	276 ± 3	[11]
2LuBr ₃ (cr) = Lu ₂ Br ₆							
846–953	12	905	308 ± 5	200 ± 5	327 ± 5	354 ± 40	This work
794–1073		907	313 ± 22		331 ± 22	326 ± 20	[11]
LuBr ₃ + LaBr ₄ [−] = LuBr ₄ [−] + LaBr ₃							
944–1011	5	973	−13.9 ± 14.4		−13.9 ± 14.4	−25.9 ± 5.0	This work
Lu ₂ Br ₇ [−] = LuBr ₄ [−] + LuBr ₃ (cr)							
913–1108	32	997	−78.4 ± 10.0		−82.2 ± 10.0	−70.5 ± 35.0	This work

Note: Given with the sign “±” are standard deviations for the values calculated by the second law of thermodynamics and limiting errors, including statistical errors and systematic errors in temperature, pressure, and reduced Gibbs energy, for the values calculated by the third law. The enthalpies and entropies of vaporization are given at 1305–1468 K, *T*_{mh} (second law). The first rows of data from [9] and [10] contain calculations from the original total saturated vapor pressures, and the second rows, calculations from the partial pressure of LuBr₃ monomers obtained from [9, 10] taking into account the ratio between monomers and dimers determined in this work.

molecular parameters for thermodynamic function calculations). This prevents us from drawing definite conclusions concerning consistency of the values obtained or their reliability. Moreover, with dimers, it was a puzzle why, in spite of the closeness of the $\Delta_s H^\circ(T_{mh})$ values (*T*_{mh} is the mean harmonic temperature) and a substantially lower $\Delta_s H^\circ(298.15)$ value found in [11] by the third law of thermodynamics, it followed from the mass spectrum reported in [11] that the fraction of dimeric molecules was about five (!) times lower than that obtained in this work.

Because of a limited number of measurements for trimeric (8.0×10^{-5} , 1.6×10^{-3} , and 3.3×10^{-3} Pa at *T* = 953, 1002, and 1021 K, respectively) and tetrameric (2.1×10^{-3} Pa at *T* = 1082 K) molecules, we could not process these results according to the second law of thermodynamics. For these molecules, the enthalpies of sublimation were estimated by the third law with the

use of the thermodynamic functions of Lu₃Br₉ and Lu₄Br₁₂ in the gas state estimated by the additivity rule with the introduction of empirical corrections [18]. The $\Delta_s H^\circ(298.15)$ values obtained were 449 ± 50 and 515 ± 50 kJ/mol for trimers and tetramers, respectively.

The enthalpies of formation of Lu_nBr_{3n}. The enthalpies of sublimation of lutetium tribromide in the form of Lu_{*n*}Br_{3*n*} (*n* = 1–4) molecules determined in this work and the enthalpy of formation of lutetium tribromide in the crystalline state, $\Delta_f H^\circ(\text{LuBr}_3, \text{cr}, 298.15 \text{ K}) = -814 \pm 10$ kJ/mol [19], were used to calculate the enthalpies of formation $\Delta_f H^\circ(298.15 \text{ K})$ of lutetium bromide mono-, di-, tri-, and tetramers. The values obtained were -538 ± 15 , -1274 ± 40 , -1993 ± 50 , and -2741 ± 50 kJ/mol, respectively.

Electron impact-induced fragmentation of LuBr₃ molecules. It was of interest to compare the degrees of fragmentation of LuBr₃ molecules under electron

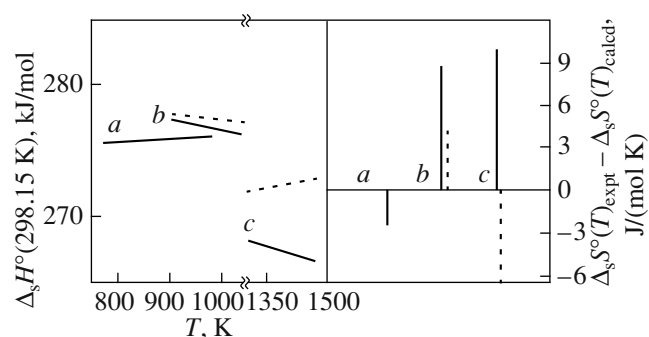


Fig. 3. Temperature dependences of $\Delta_s H^\circ(\text{LuBr}_3, 298.15 \text{ K})$ and the difference $\Delta_s S^\circ(\text{LuBr}_3, T)_{\text{expt}} - \Delta_s S^\circ(\text{LuBr}_3, T)_{\text{calcd}}$: (a) our data, (b) data from [10], and (c) data from [9]. The results of calculations performed using the original total vapor pressure data [9, 10] and vapor pressures recalculated taking into account the contribution of dimeric molecules are shown by solid and dashed lines, respectively.

impact in two sublimation regimes. The probability of observing differences can be predicted from the following considerations. An adsorbed molecule on the surface of a crystal that experiences sublimation is in an electric field of an excess surface charge concentrated at vaporization steps (e.g., see [20–22]) and is therefore polarized to a certain degree. Earlier, we found that the temperature dependences of the degree of alkali metal halide molecule fragmentation correlated with the field strength of a surface charge of the defect-impurity nature [23, 24]. The conclusion was drawn that molecules that sublime from an open ionic crystal surface could possess “superthermal” rotational-vibrational excitation.

This effect is based on the transformation of Stark energy caused by the appearance of an induced dipole moment of an adsorbed molecule into vibrational and/or rotational excitation energy of the molecule as it leaves the zone of the influence of the surface charge. Unfortunately, there are no literature data on the thermodynamic properties of separate point defects on the surface of LnX_3 , and the problem can therefore be analyzed at a qualitative level only. The value that can conveniently be analyzed is the relative partial ionization cross section Φ ; Φ is the ratio between the current of ions of a given type to the total current of all ions formed from molecules under consideration when electron and molecular beams interact.

The temperature dependence of Φ for single-charged ions calculated for the Knudsen and Langmuir regimes are shown in Fig. 4. We see that, indeed, these data differ and their temperature dependences are also slightly different. In particular, the relative partial ionization cross section for LuBr_2^+ ions is slightly lower under Langmuir conditions. According to Fig. 4, this decrease is accompanied by an increase in the efficiency of formation of LuBr_3^+ molecular ions under

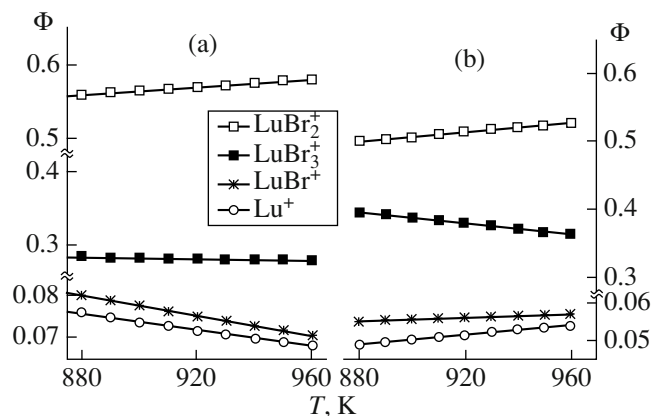


Fig. 4. Temperature dependences of the relative partial ionization cross sections Φ of LuBr_3 molecules under electron impact: (a) Knudsen and (b) Langmuir sublimation conditions.

electron impact. According to our interpretation, a key factor is an increase in the vibrational excitation of molecules that sublime from an open single crystal surface under the influence of a surface charge field. Because of the population of higher vibrational levels of the molecule as a result of anharmonicity of vibrations, the probability of Frank–Condon transitions resulting in the formation of stable molecular ions should increase. Relative excess vibrational excitation, however, likely decreases as the temperature increases, which results in a noticeable decrease in Φ for molecular ions. At the same time, the Φ values for Lu^+ and LuBr^+ decrease under Langmuir vaporization conditions and change in the directions different from those observed under Knudsen conditions. These ions are likely formed via electronically excited LuBr_3^+ ion states [25].

The relative concentrations of dimeric and monomeric molecules. The mass spectrum recorded under Langmuir sublimation conditions is evidence that Lu_2Br_6 dimeric molecules are also present in the sublimation flux from the open surface of a LuBr_3 single crystal. The activation energies of sublimation from the lutetium tribromide crystal in the form of monomers and dimers were determined from the regression coefficients of the dependences $\log(\sum_j I_j T / a_j \gamma_j) - 1/T$ (j : Lu^+ , LuBr^+ , LuBr_2^+ , LuBr_3^+ , Lu^{++} , LuBr^{++} , and LuBr_2^{++}) and $\log I_{\text{Lu}_2\text{Br}_6} T - 1/T$. This gave $E_s(\text{LuBr}_3, 918 \text{ K}) = 299 \pm 3 \text{ kJ/mol}$ and $E_s(\text{Lu}_2\text{Br}_6, 938 \text{ K}) = 342 \pm 15 \text{ kJ/mol}$. As distinct from lanthanum tribromide studied in [8], whose enthalpy and activation energy of sublimation were equal to within measurement errors, the activation energies of sublimation of LuBr_3 in the form of monomers and dimers were higher than the corresponding enthalpies of sublimation. This difference can be explained by a change in the structure of kinks

(kinks of vaporization steps) on the surface of lutetium tribromide under different sublimation conditions. It should, however, be borne in mind that the energy characteristics of sublimation under Langmuir conditions are “apparent” values. The “true” activation energy of sublimation can be obtained if the temperature dependence of the α_s sublimation coefficient can be ignored. The α_s value is in turn determined by several factors primarily depending on the structural and electric properties of the surface of the ionic crystal [24].

The absolute α_s values for monomers and dimers could not be determined by the method that we used. Relative changes in the sublimation coefficients are, however, easy to analyze by comparing the ratios of the fluxes of molecules. For instance, the $j(\text{Lu}_2\text{Br}_6)/j(\text{LuBr}_3)$ ratios between fluxes from the surface of LuBr_3 crystals under Knudsen and Langmuir conditions at 1000 K are 7.07×10^{-2} and 1.77×10^{-2} , respectively; that is, the fraction of sublimed dimeric molecules decreases by a factor of about four in passing from dynamically equilibrium sublimation conditions to open surface vaporization. In other words, this factor is an estimate of the ratio between the sublimation coefficients for dimers $\alpha_s(\text{Lu}_2\text{Br}_6)$ and monomers $\alpha_s(\text{LuBr}_3)$. A formal analysis of the ratio between the sublimation coefficients of dimers and monomers can be performed using the quasi-thermodynamic approach [26] on the basis of the equation

$$\frac{\alpha_s(\text{Lu}_2\text{Br}_6)}{\alpha_s(\text{LuBr}_3)} = \exp \{ - [\Delta_s H^*(\text{Lu}_2\text{Br}_6) - \Delta_s H^*(\text{LuBr}_3)]/RT - [\Delta_s H^\circ(\text{Lu}_2\text{Br}_6) - \Delta_s H^\circ(\text{LuBr}_3)]/RT + [\Delta_s S^*(\text{Lu}_2\text{Br}_6) - \Delta_s S^*(\text{LuBr}_3)]/R - [\Delta_s S^\circ(\text{Lu}_2\text{Br}_6) - \Delta_s S^\circ(\text{LuBr}_3)]/R \}. \quad (6)$$

Here, R is the universal gas constant and $\Delta_s H^*$ and $\Delta_s S^*$ are the enthalpy and entropy of activation of sublimation, respectively (in a first approximation, the E_a and $\Delta_s H^*$ values are assumed to be equal). The $\Delta_s H^\circ(\text{Lu}_2\text{Br}_6) - \Delta_s H^\circ(\text{LuBr}_3) = 48 \pm 5$ kJ/mol and $\Delta_s H^*(\text{Lu}_2\text{Br}_6) - \Delta_s H^*(\text{LuBr}_3) = 43 \pm 15$ kJ/mol increments have similar values. Their difference can be taken to be zero to within measurement errors. It follows that, as with LaBr_3 , the difference between $\alpha_s(\text{Lu}_2\text{Br}_6)$ and $\alpha_s(\text{LuBr}_3)$ cannot be explained by energy considerations.

From the point of view of the entropy factor, sublimation can be decelerated ($\Delta_s S^* < \Delta_s S^\circ$) for several reasons, including (1) slow surface diffusion of molecules into desorption positions, (2) hindered rotation of molecules in the adsorbed state on the surface compared with free rotation in the gas phase, and (3) different molecular structures on the surface of a crystal and in the gas phase [26]. The first reason can be a consequence of the special features of the morphological development of the surface of a crystal, and key param-

eters determining sublimation coefficient values are the distance between vaporization steps λ and the mean displacement of a particle during surface self-diffusion d [27, 28],

$$\alpha_s = \frac{d}{\lambda} \tanh\left(\frac{\lambda}{d}\right). \quad (7)$$

The kinetic parameter d is determined by the equation [29]

$$d = r \exp[(E_{\text{des}} - E_{\text{diff}})/(2kT)], \quad (8)$$

where r is the mean diffusion jump length and E_{diff} and E_{des} are the activation energies of self-diffusion of a particle on surface terraces and desorption from them, respectively. The determination of d and λ is a complex experimental problem involving combined use of the molecular beam and electron or atomic-force microscopy methods. At present, this problem has been solved for the simplest cubic crystals (e.g., see [30]). So far as we know, such information is completely absent for lanthanide halides. Nevertheless, we are interested in relative rather than absolute monomer and dimer sublimation rates under the Knudsen and Langmuir conditions. It is therefore pertinent to mention several points.

Since the surface diffusion of adsorbed molecules under Langmuir conditions occurs in the electric field of a surface crystal charge, the activation energy of diffusion depends substantially on the polarizability of molecules, which, according to experimental studies [31], is much larger for gas phase dimers than for monomers. It is reasonable to assume that the polarizability of Ln_2X_6 is also higher than that of LnX_3 . As a consequence, the activation energy of surface diffusion is higher for dimers. It follows that the surface diffusion of dimers is decelerated to a greater extent than the surface diffusion of monomers in the passage from Knudsen to Langmuir sublimation conditions.

From the point of view of the difference of the partial sublimation coefficients of monomers and dimers, the second and third reasons specified above can play an important role. In considering these factors, an important role can again be played by a surface charge electric field, which hinders rotation and distorts the structure of adsorbed molecules because of its polarizing action. Just these factors can be the reason for the difference in entropy increments of dimers and monomers in (6).

Ionic sublimation. Under both sublimation conditions, we observed the thermal emission of the LuBr_4^- and Lu_2Br_7^- negative ions.² Under Knudsen conditions, the mass spectra also contained Br^- ions formed predominantly on the outside effusion cell surface; the $\text{Lu}_3\text{Br}_{10}^-$ ions were also recorded at the sensitivity

² We do not take into account the emission of positive alkali metal ions present as impurity, which are always observed.

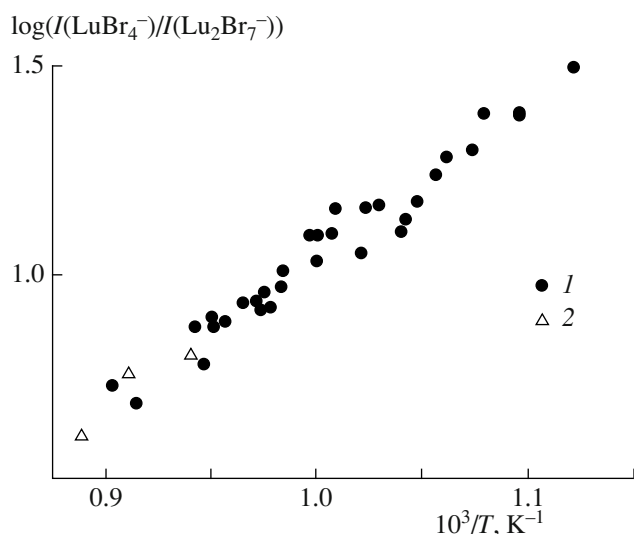
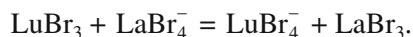


Fig. 5. Dependences of the ratio between LuBr_4^- and Lu_2Br_7^- ion currents on inverse temperature under (1) Knudsen and (2) Langmuir sublimation conditions.

threshold. The “extraneous” origin of Br^- ions [8] prevents us from using them in constructing ion-molecular reactions for the determination of the enthalpies of formation of negative ions emitted directly by the substance studied. For this purpose, we performed an additional experiment with the LaBr_3 – LuBr_3 binary system to determine the equilibrium constant of the gas-phase exchange reaction



In this reaction, the LaBr_4^- ion plays the role of a reference; the enthalpy of its formation $\Delta_f H^\circ(\text{LaBr}_4^-, \text{g}, 298.15 \text{ K}) = -1105 \pm 14 \text{ kJ/mol}$ was reliably established by us in [8]. The calculated enthalpies of this reaction are given in Table 4 (the procedure for calculating the enthalpies of exchange reactions is described in detail, e.g., in [32]). These data were used to obtain $\Delta_f H^\circ(\text{LuBr}_4^-, \text{g}, 298.15 \text{ K}) = -1085 \pm 23 \text{ kJ/mol}$.

The enthalpy of formation of Lu_2Br_7^- ions was determined by studying the heterophase reaction

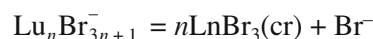


The enthalpies of this reaction found using the second and third laws of thermodynamics are listed in Table 4. They were used to determine the enthalpy of formation of Lu_2Br_7^- ions, $\Delta_f H^\circ(\text{Lu}_2\text{Br}_7^-, \text{g}, 298.15 \text{ K}) = -1829 \pm 40 \text{ kJ/mol}$. The thermodynamic functions of the LuBr_4^- , LaBr_4^- , and Lu_2Br_7^- ions used in the calculations are given by the coefficients of (5) listed in Table 3. The

functions of LuBr_4^- and LaBr_4^- were calculated in the rigid rotator–harmonic oscillator approximation with the use of the molecular constants obtained in nonempirical calculations of the structure, force fields, and vibrational spectra of LnX_4^- ions [33, 34]. The functions of Lu_2Br_7^- were estimated according to the additivity rule with the introduction of an empirical correction [18]. We used the following literature data on the enthalpies of formation $\Delta_f H^\circ(298.15 \text{ K})$: -584 ± 10 (LaBr_3) [8, 19], -1105 ± 14 (LaBr_4^-) [34], and $-904.4 \pm 1.5 \text{ kJ/mol}$ (LaBr_3, cr) [19].

The $\log I(\text{LuBr}_4^-) - 1/T$ dependences measured under Knudsen and Langmuir conditions were used to determine the enthalpy and activation energy, respectively, of sublimation of LuBr_4^- ions, $\Delta_s H^\circ(\text{LuBr}_4^-, 1058 \text{ K}) = 260 \pm 17 \text{ kJ/mol}$ and $E_s(\text{LuBr}_4^-, 1066 \text{ K}) = 318 \pm 23 \text{ kJ/mol}$. It follows that the difference between the $\Delta_s H^\circ$ and E_s values is approximately the same for the LuBr_4^- ions and LuBr_3 molecules, which corresponds to similar effects of the structural rearrangement of the surface in the passage from the conditions of dynamic equilibrium with saturated vapor to free sublimation conditions.

Our preceding study of lanthanum tribromide [8] led us to conclude that studies of ionic sublimation from the surface of a single crystal with the use of a drawing out collimating electrode fully suppressed “extraneous” ion signals. We did not observe the signal of Br^- ions for lutetium tribromide under Langmuir vaporization conditions, which substantiated the above conclusion. Another important problem is the establishment of ion-molecular equilibria such as



on the open surface of a single crystal. The equality of the ion current ratios $I(\text{LuBr}_4^-)/I(\text{Lu}_2\text{Br}_7^-)$ at various temperatures under equilibrium and free sublimation conditions is evidence that equilibrium was established. A similar effect was observed for LaBr_3 [8]. In this study, the $I(\text{LuBr}_4^-)/I(\text{Lu}_2\text{Br}_7^-)$ ratio can also be considered unchanged in the passage from Knudsen to Langmuir conditions (Fig. 5). Note only that emitted ion currents were noticeably weaker under Langmuir conditions than under Knudsen conditions. We therefore only made three measurements of this ratio at temperatures which already exceeded the pressure limit (10 Pa) for effusion measurements.

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