

# Mass-Spectrometric Study of Molecular and Ionic Sublimation of Gadolinium and Terbium Tribromides in Knudsen and Langmuir Modes

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**Abstract**—Molecular and ionic sublimation of gadolinium and terbium tribromides in Knudsen and Langmuire modes was studied by the method of high-temperature mass-spectrometry. On the basis of obtained enthalpies of sublimation and ion-molecule reactions the enthalpies of formation of  $\text{LnBr}_3$  and  $\text{Ln}_2\text{Br}_6$  molecules and  $\text{LnBr}_4^-$  and  $\text{Ln}_2\text{Br}_7^-$  negative ions were determined. For the first time the electron work function for crystals of the studied tribromides was calculated.

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The systematic study of thermodynamics and kinetics of the molecular and ionic sublimation of tribromide of certain lanthanides was started in [1–6].

Saturated vapor pressures above  $\text{GdBr}_3$  and  $\text{TbBr}_3$  were measured earlier by the boiling point [7, 8], mass-spectrometry [9], and torsion-effusion [10] methods, and also by the static methods [11] ( $\text{GdBr}_3$ ). Except for [9], where dimeric molecules were detected in vapor, in the above-mentioned works the total pressure was measured, and the data were treated on the assumption that only monomeric molecules are present in the vapor.

In this work new experimental data on the vapor pressure together with available published data including an updated set of thermodynamic functions were used for the calculation of the enthalpy of sublimation of gadolinium and terbium tribromides in the form of monomeric and dimeric molecules. On the basis of the examination of the obtained results thermodynamic parameters of monomeric and dimeric molecules were recommended.

Thermodynamics of ionic sublimation of the specified tribromides was studied for the first time, equilibrium constants were measured and enthalpies of ion-molecule reactions were calculated, and enthalpies of formation of negative ions  $\text{LnBr}_4^-$  and  $\text{Ln}_2\text{Br}_7^-$

(hereinafter  $\text{Ln} = \text{Gd}, \text{Tb}$ ) were determined on their basis.

In addition to the thermodynamic studies we have studied for the first time the kinetics of sublimation of  $\text{GdBr}_3$  and  $\text{TbBr}_3$  single crystals in Langmuir mode (evaporation from an open surface) and have determined the activation energies of their sublimation in the form of monomeric and dimeric molecules and also of negative ions  $\text{LnBr}_4^-$  and  $\text{Ln}_2\text{Br}_7^-$  in Knudsen mode (evaporation under equilibrium conditions) from temperature dependences of ionic currents.

*Measurements of molecular sublimation in Knudsen mode.* In the mass spectra of vapor above gadolinium and terbium tribromides (Table 1) in the temperature ranges 878–1044 and 860–1067 K, respectively, similarly to other tribromides [1–6, 9], the following ions were identified:  $\text{Ln}^+$ ,  $\text{LnBr}^+$ ,  $\text{LnBr}_2^+$ ,  $\text{LnBr}_3^+$ ,  $\text{Ln}_2\text{Br}_4^+$ ,  $\text{Ln}_2\text{Br}_5^+$ , and  $\text{Tb}_3\text{Br}_8^+$ . Except for the enumerated ions, two-charge ions  $\text{Ln}^{++}$ ,  $\text{LnBr}^{++}$ , and  $\text{LnBr}_2^{++}$  making a ~3% contribution to the total ionic current were recorded.

The standard procedure of correlating detected ions to their molecular precursors [analysis of forms of ionization effectiveness curves (IEC) for various ions, measuring appearance energies of ions by the method of linear extrapolation of IEC near-threshold sections (Table 1), and determination of coefficients of tem-

**Table 1.** Mass spectra taken at the ionization by electrons in Knudsen and Langmuir modes and appearance energies of ions (AE)

Value	Mode	Ln <sup>+</sup>	LnBr <sup>+</sup>	LnBr <sub>2</sub> <sup>+</sup>	LnBr <sub>3</sub> <sup>+</sup>	Ln <sub>2</sub> Br <sub>4</sub> <sup>+</sup>	Ln <sub>2</sub> Br <sub>5</sub> <sup>+</sup>	References
GdBr <sub>3</sub> (T 901 K) <sup>a</sup>								
Relative ionic current I <sub>i</sub> <sup>b</sup> , %	Knudsen	11.1	9.9	100	41.0	0.7	9.2	This work
	Langmuir	11.6	7.4	100	12.5		0.6	
AE, eV		19.9	14.3	11.6	10.0		10.4	This work [9]
		20.1	15.2	11.3	10.5		11.0	
TbBr <sub>3</sub> (T 905 K)								
Relative ionic current I <sub>i</sub> , %	Knudsen	23.1	14.2	100	45.9	0.1	6.3	This work
	Langmuir	16.7	20.7	100	32.3	0.2	2.9	
AE, eV		18.8	14.3	11.0	10.2		11.6	This work [9]
		19.7	15.1	11.3	10.5		11.1	

<sup>a</sup> Appearance energies of the two-charge ions Gd<sup>++</sup> and GdBr<sup>++</sup> were 34.0 and 30.6 eV, respectively. <sup>b</sup> The values of relative ionic currents are given in view of natural isotope varieties of ions and corrections for the dependence of the coefficient on the ion-electron conversion of the secondary-emission multiplier  $\mu$  on the ion mass (see the text).

**Table 2.** Coefficients of the equation  $\log p(\text{Pa}) = -A \times 10^3/T + B$ 

Ln	LnBr <sub>3</sub>			Ln <sub>2</sub> Br <sub>6</sub>		
	T, K	A	B	T, K	A	B
Gd	878–1044	14.43±0.35	14.99±0.37	907–1043	18.74±0.57	18.02±0.61
Tb	860–1064	14.29±0.27	14.44±0.29	898–1063	18.46±0.37	17.33±0.37

perature dependences of ionic currents] suggested that ions with one lanthanide atom are formed preferentially on the ionization of monomeric molecules LnBr<sub>3</sub>, whereas the ions Ln<sub>2</sub>Br<sub>4</sub><sup>+</sup>, Ln<sub>2</sub>Br<sub>5</sub><sup>+</sup>, and Tb<sub>3</sub>Br<sub>8</sub><sup>+</sup> are products of the dissociative ionization of dimeric molecules Ln<sub>2</sub>Br<sub>6</sub> and trimeric molecules Tb<sub>3</sub>Br<sub>9</sub>, respectively.

Partial pressures of molecules ( $p_i$ ) in vapor were calculated by Eq. (1).

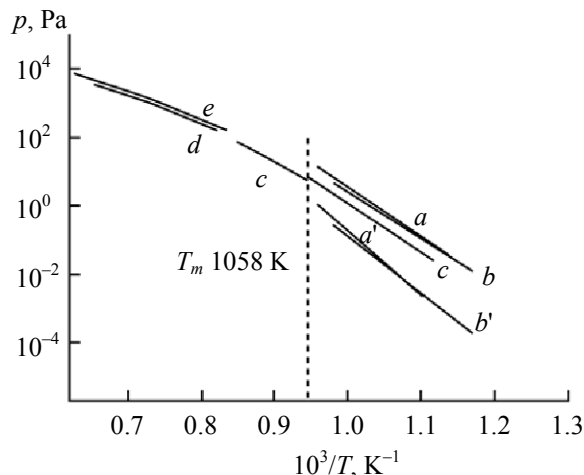
$$p_i = \frac{kI_i T}{\sigma_i^{\text{mol}}} \quad (1)$$

Here ( $k$ ) is a constant of the instrument sensitivity (determined in a special experiment on the vaporization of metal silver), ( $T$ ) is a temperature of a cell,  $I_i = \sum I_j / (a_j \gamma_j)$  is a total ionic current of all types of ions formed by the  $i$ th molecule, ( $a$ ) is a coefficient considering natural abundance of isotopes of the measured ion, ( $\gamma$ ) is a coefficient of the ion-electron conversion {we accepted  $\gamma \sim M^{-1/2}$  [12], ( $M$ ) is a molecular weight of an ion}, ( $\sigma_i^{\text{mol}}$ ) is a total cross-

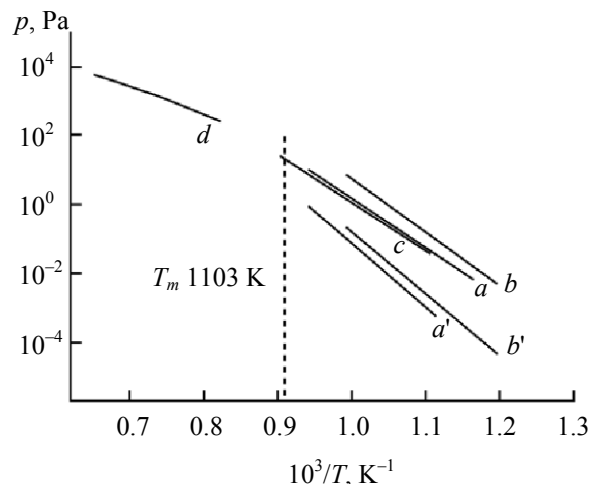
section of the  $i$ th molecule ionization at the working energy of ionizing electrons (calculated on the basis of the ionization cross-sections of atoms  $\sigma^{\text{at}}$  [13] by the expression  $\sigma^{\text{mol}} = 0.75 \sum \sigma_j^{\text{at}}$  [14]).

Temperature dependences of saturated vapor pressures of monomeric and dimeric molecules are approximated by linear equations  $\log p = -A \times 10^3/T + B$  with the coefficients given in Table 2.

Partial pressures of components of saturated vapor above gadolinium and terbium tribromides together with the mass-spectrometric data of [9], and also with the data on the total pressure [7, 8, 10, 11] are shown in Figs. 1 and 2. It is seen from the figures that all the data on vapor pressures above GdBr<sub>3</sub> and TbBr<sub>3</sub> are located within the limits not exceeding an order of magnitude. For GdBr<sub>3</sub> our data agree better with the mass-spectrometric data [9], and for TbBr<sub>3</sub> – with the data obtained by the effusion-torsion method [10]. In the latter case our data on the pressures of both monomers and dimers are lower by a factor 2–3 than the pressures measured in [9], whereas the monomer:



**Fig. 1.** Temperature dependences of vapor pressure above  $\text{GdBr}_3$ : (a) monomer, (a') dimer, this work, (b) monomer, (b') dimer, [9], (c) [11], (d) [8, 9], (e) [7].



**Fig. 2.** Temperature dependences of vapor pressure above  $\text{TbBr}_3$ : (a) monomer, (a') dimer, this work, (b) monomer, (b') dimer, [9], (c) [11], (d) [8, 9].

dimer ratios in the both works are close to each other. The fraction of dimeric molecules in the studied temperature range for the studied tribromides does not exceed 6%.

Enthalpies of  $\text{LnBr}_3$  sublimation in the form of monomeric and dimeric molecules were calculated by Eqs. (2) and (3).

$$\Delta_r H^0(T) = -R \frac{\partial \ln K_p(T)}{\partial (1/T)}, \quad (2)$$

$$\Delta_r H^0(0) = T[\Delta_r \Phi^0(T) - R \ln K_p(T)]. \quad (3)$$

Here  $\Delta_r H^0(0)$ ,  $\Delta_r H^0(T)$ , and  $\Delta_r \Phi^0(T)$  are changes of the reaction enthalpy and the reduced Gibbs energy at temperatures 0 and  $T$  K, respectively, ( $R$ ) the gas constant, and ( $K_p$ ) is the reaction equilibrium constant.

Thermodynamic functions of  $\text{TbBr}_3$  in the condensed state necessary for the calculations were taken from [15] and those of  $\text{GdBr}_3$ , from the database [16]. Thermodynamic functions of monomeric  $\text{LnBr}_3$  molecules in the ideal gas state were calculated in the "rigid rotator–harmonic oscillator" approximation using molecular constants recommended on the basis of the examination of available results of the experimental and theoretical studies [17]. Functions of  $\text{Ln}_2\text{Br}_6$  dimeric molecules were estimated by a comparative method by analogy with  $\text{Lu}_2\text{Br}_6$  [2]. The thermodynamic functions used in the calculations are given in Table 3.

The results of processing the whole combination of the experimental data fulfilled with the use of a

uniform set of thermodynamic functions are presented in Table 4. In the calculation of the sublimation enthalpies of monomers the data of [7, 8, 10, 11] on total pressure were corrected for the vapor composition obtained from mass-spectrometry measurements. As a whole, as it is seen from Table 4, the values of sublimation enthalpies of monomers and dimers calculated by two independent methods using data of different authors agree within the limits of errors. The weighted average values (Table 5) found on the basis of criteria analysis [2] have been accepted as recommended values. As criteria (accepted equivalent) we have selected: (a) temperature run of the values of sublimation enthalpies calculated by Eq. (3); (b) comparison of sublimation entropies determined experimentally by Eq. (2) and calculated theoretically.

The enthalpies of formation of monomeric and dimeric molecules, which are presented in Table 5, were found by combining accepted values of the sublimation enthalpies and of the enthalpies of formation of gadolinium and terbium tribromides in the crystalline state [18].

*Measurements of ionic sublimation in Knudsen mode.* The ions  $\text{Br}^-$ ,  $\text{LnBr}_4^-$ , and  $\text{Ln}_2\text{Br}_7^-$  were recorded for the both tribromides in the mass spectra of the ionic sublimation in the range 860–1070 K. The ions  $\text{LnBr}_4^-$  were most intensive in the mass spectra, the intensity of the ions  $\text{Ln}_2\text{Br}_7^-$  was less by approximately an order of magnitude. The intensity of the current of the atomic ion  $\text{Br}^-$  was from 2 up to 5% of the  $\text{LnBr}_4^-$  intensity.

**Table 3.** Thermodynamic functions (A)  $\Phi^0(T)$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ) and (B)  $H^0(T) - H^0(0)$  ( $\text{kJ mol}^{-1}$ ) used in calculations of sublimation enthalpies<sup>a</sup>

$T, \text{K}$	GdBr <sub>3</sub> (cr.)		GdBr <sub>3</sub> (gas)		Gd <sub>2</sub> Br <sub>6</sub> (gas)		GdBr <sub>4</sub> <sup>-</sup> (gas)		Gd <sub>2</sub> Br <sub>7</sub> <sup>-</sup> (gas)	
	A	B <sup>b</sup>	A	B	A	B	A	B	A	B
298	189.96	0	333.42	20.49	514.78	44.63	367.90	26.58	540.89	51.27
700	218.06	40.86	395.66	53.44	649.23	117.25	447.59	69.53	692.24	134.89
800	226.27	51.36	405.91	61.71	672.16	135.46	461.19	80.28	718.13	155.84
900	234.11	61.99	415.03	69.99	692.68	153.68	473.36	91.05	741.32	176.80
1000	241.57	72.68	423.25	78.28	711.14	171.91	484.31	101.83	762.18	197.78
$T, \text{K}$	TbBr <sub>3</sub> (cr.) <sup>b</sup>		TbBr <sub>3</sub> (gas)		Tb <sub>2</sub> Br <sub>6</sub> (gas)		TbBr <sub>4</sub> <sup>-</sup> (gas)		Tb <sub>2</sub> Br <sub>7</sub> <sup>-</sup> (gas)	
	A	B <sup>b</sup>	A	B	A	B	A	B	A	B
298	194.02	0	337.48	20.45	527.58	45.55	372.36	26.53	554.92	52.29
700	221.49	39.79	398.63	53.41	658.54	118.27	452.01	69.48	702.66	136.06
800	229.45	49.89	409.10	61.68	681.16	136.48	465.61	80.24	728.17	157.02
900	237.06	60.07	418.48	69.96	701.34	154.71	477.78	91.01	751.06	177.09
1000	244.29	70.33	426.91	78.24	719.53	172.96	488.72	101.79	771.68	198.98

<sup>a</sup> Errors in Gibbs energy functions were estimated by a procedure proposed in [14] and were accepted to be ( $T = 1000 \text{ K}$ ):  $\pm 12$  (LnBr<sub>3</sub>),  $\pm 14$  (LnBr<sub>4</sub><sup>-</sup>),  $\pm 40$  (Ln<sub>2</sub>Br<sub>6</sub>), and  $\pm 45 \text{ J mol}^{-1} \text{K}^{-1}$  (Gd<sub>2</sub>Br<sub>7</sub><sup>-</sup>). <sup>b</sup>  $H^0(T) - H^0(298)$  is given.

**Table 4.** Values of enthalpies ( $\text{kJ mol}^{-1}$ ) and entropies ( $\text{J mol}^{-1} \text{K}^{-1}$ ) of GdBr<sub>3</sub> sublimation in the form of monomeric and dimeric molecules determined by Eqs. (2) and (3)<sup>a</sup>

$T, \text{K}$	$N$	$T_{\text{cr}}$	(2)			(3)		References
			$\Delta_s H^0(T_{\text{cr}})$	$\Delta_s S^0(T_{\text{cr}})$	$\Delta_s H^0(298 \text{ K})$	$\Delta_s H^0(298 \text{ K})$	$\Delta_s S^0(T_{\text{cr}})$	
GdBr <sub>3</sub> (cr.) = GdBr <sub>3</sub> (gas)								
878–1044	26	954	276.3±6.7	191.3±7.1	290.0±6.7	288±12	189±12	This work
854–1020	45	937	261.6±3.8	173.9±4.0	274.9±3.8	289±2	189±12	[9]
895–1057	102	976	271.0±3.8	176.6±3.9	285.3±3.8	296±12	188±12	[10]
1060–1179	32	1120	229.0±3.8	134.7±3.9	287.0±3.8	299±12	137±12	
1220–1532		1376	203.8	116.2	276.3	301±12	125±12	[7, 8]
1200–1600		1400	198.0	114.2	277.6	300±12	124±12	[11]
2GdBr <sub>3</sub> (cr.) = Gd <sub>2</sub> Br <sub>6</sub> (gas)								
907–1043	21	967	358.8±10.9	249.3±11.7	375.8±10.9	382±40	255±40	This work
854–1020	45	937	319.3±8.1	206.7±7.7	335.3±8.1	382±40	256±40	[9]
TbBr <sub>3</sub> (cr.) = TbBr <sub>3</sub> (gas)								
860–1064	23	954	273.6±5.2	180.7±7.7	282.4±5.2	296±12	194±12	This work
836–1008	102	922	279.6±3.8	194.5±3.9	290.6±3.8	288±12	192±2	[9]
904–1108	127	1006	262.9	167.9	275.6	298±12	190±12	[10]
1219–1536		1378	198.0	115.3	267.1	302±12	140±12	[7, 8]
2TbBr <sub>3</sub> (cr.) = Tb <sub>2</sub> Br <sub>6</sub> (gas)								
898–1063	15	985	353.5±7.1	236.1±7.1	367.6±7.1	394±40	264±40	This work
836–1008	45	922	345.0±8.1	233.8±7.7	357.6±8.1	385±40	265±40	[9]

<sup>a</sup> ( $N$ ) is the number of measurements; ( $T_{\text{av}}$ ) average harmonic temperature,  $T_{\text{av}} = N/\Sigma(1/T_i)$ . In [7, 8, 11] the saturated vapor pressure was measured above liquid LnBr<sub>3</sub>. For the values calculated by Eq. (2) with the sign “±” the standard deviation is given; by Eq. (3), the limiting error taking into account a statistical error and systematic errors in temperature, pressure, and reduced Gibbs energy functions.

**Table 5.** Thermodynamic and kinetic parameters of sublimation and enthalpies of formation of molecules and ions (kJ mol<sup>-1</sup>)

Parameter	Gd	Tb
$\Delta_s H^\circ(\text{LnBr}_3, \text{cr.}, 298 \text{ K})$	294±5	291±5
$\Delta_s H^\circ(\text{Ln}_2\text{Br}_6, \text{cr.}, 298 \text{ K})$	380±28	391±28
$\Delta_f H^\circ(\text{LnBr}_3, \text{gas}, 298 \text{ K})$	-544±6	-553±6
$\Delta_f H^\circ(\text{Ln}_2\text{Br}_6, \text{gas}, 298 \text{ K})$	-1296±30	-1296±30
$\Delta_s H^\circ(\text{LnBr}_4^-, \text{cr.}, T)$	273±12 (900 K)	280±8 (1000 K)
$\Delta_s H^\circ(\text{Ln}_2\text{Br}_7^-, \text{cr.}, T)$	397±53 (920 K)	386±11 (1050 K)
$\Delta_f H^\circ(\text{LnBr}_4^-, \text{gas}, 298 \text{ K})$	-1077±17 <sup>a</sup>	-1084±27
$\Delta_f H^\circ(\text{Ln}_2\text{Br}_7^-, \text{gas}, 298 \text{ K})$	-1831±44	-1832±44
$E_a(\text{LnBr}_3, \text{cr.}, T)$	279±7 (980 K)	283±7 (1000 K)
$E_a(\text{Ln}_2\text{Br}_6, \text{cr.}, T)$	397±15 (970 K)	375±15 (1000 K)
$E_a(\text{LnBr}_4^-, \text{cr.}, T)$	284±12 (930 K)	305±18 (1030 K)
$E_a(\text{Ln}_2\text{Br}_7^-, \text{cr.}, T)$	383±32 (935 K)	393±15 (1035 K)

<sup>a</sup> The value averaged over two reactions (Table 6) is given.

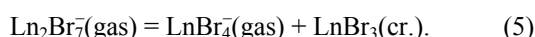
Enthalpies of sublimation of tribromides in the form of the  $\text{LnBr}_4^-$  and  $\text{Ln}_2\text{Br}_7^-$  ions for the average temperature of the experiment were determined from the temperature dependences of ionic currents  $\log IT^{1/2} = f(1/T)$ , which are presented in Table 5. To determine the enthalpies of formation of  $\text{LnBr}_4^-$  ions, a procedure based on measuring the equilibrium constant of gas-phase ion-molecular reaction (4) for systems with various lanthanides  $\text{Ln}^{\text{I}}$  and  $\text{Ln}^{\text{II}}$  was used.



In this reaction the ion  $\text{Ln}^{\text{I}}\text{Br}_4^-$  acts as a standard, and the formation enthalpy of the ion  $\text{Ln}^{\text{II}}\text{Br}_4^-$  was determined in relation to it.

To realize this procedure, we have studied the binary system  $\text{LuBr}_3\text{-GdBr}_3$  and two ternary systems  $\text{LaBr}_3\text{-GdBr}_3\text{-LuBr}_3$  and  $\text{LaBr}_3\text{-TbBr}_3\text{-YbBr}_3$ , using the enthalpies of formation of the  $\text{LuBr}_4^-$  and  $\text{LaBr}_4^-$  ions as standards. The equilibrium constants of reactions (4) measured at various temperatures and the enthalpies of reactions (4) calculated by Eqs. (2) and (3) are presented in Table 6.

Enthalpies of formation of ions were determined on the basis of equilibrium constants measured of reaction (5) while studying pure gadolinium and terbium tribromide.

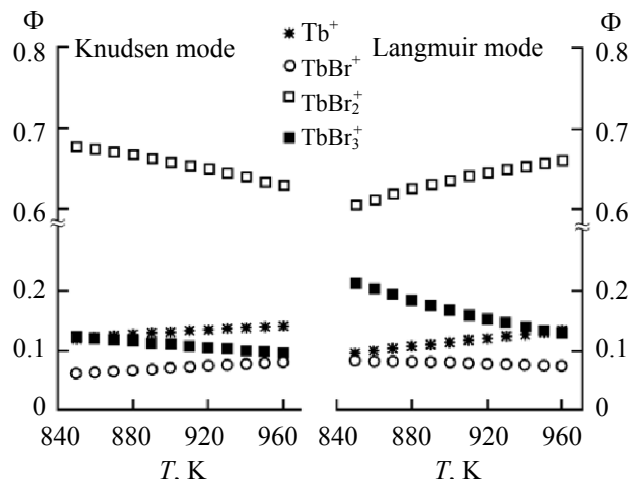

**Table 6.** Experimental values of equilibrium constants and enthalpies of the ion-molecular reactions determined by Eqs. (2) and (3)

Process <sup>a</sup>	T, K	$\ln K_p^0$	$\Delta_f H^\circ(298 \text{ K}), \text{kJ mol}^{-1}$	
I	877	2.174	-13.9±14.4 (2)	
	912	2.550	-16.6±5.0 (3)	
	944	2.440		
	958	2.100		
II	870	-1.559	17.7±19.1 (2)	
	881	-1.484	18.7±5.0 (3)	
	902	-1.333		
	906	-1.164		
	922	-1.354		
	944	-1.849		
	950	-1.024		
	984	-1.110		
	III	938	1.684	-10.3±9.2 (2)
		976	1.458	-10.4±5.0 (3)
994		1.663		
1017		1.317		
1040		1.268		
IV	1152	1.451		
	889	2.260	-90±62 (2)	
	893	4.135	-79±35 (3)	
	902	3.772		
	909	2.585		
	925	2.797		
	934	2.940		
	947	2.575		
V	970	2.113		
	1025	3.610	-96±30 (2)	
	1029	3.392	-96±35 (3)	
	1034	3.186		
	1047	3.186		
	1065	3.096		
	1070	3.082		

<sup>a</sup>  $\text{GdBr}_3(\text{gas}) + \text{LaBr}_4^-(\text{gas}) \rightarrow \text{LaBr}_3(\text{gas}) + \text{GdBr}_4^-(\text{gas})$  (I);  $\text{GdBr}_3(\text{gas}) + \text{LuBr}_4^-(\text{gas}) \rightarrow \text{LuBr}_3(\text{gas}) + \text{GdBr}_4^-(\text{gas})$  (II);  $\text{TbBr}_3(\text{gas}) + \text{LaBr}_4^-(\text{gas}) \rightarrow \text{LaBr}_3(\text{gas}) + \text{TbBr}_4^-(\text{gas})$  (III);  $\text{Gd}_2\text{Br}_7^-(\text{gas}) \rightarrow \text{GdBr}_3(\text{cr.}) + \text{GdBr}_4^-(\text{gas})$  (IV);  $\text{Tb}_2\text{Br}_7^-(\text{gas}) \rightarrow \text{TbBr}_3(\text{cr.}) + \text{TbBr}_4^-(\text{gas})$  (V).

The input data and the results of their processing are presented in Table 6.

Thermodynamic functions of  $\text{LnBr}_4^-$  and  $\text{Ln}_2\text{Br}_7^-$  ions in the ideal gas state (Table 3) necessary for the calculations were calculated by the procedure given in [2]. The enthalpies of formation of  $\text{LnBr}_4^-$  and  $\text{Ln}_2\text{Br}_7^-$

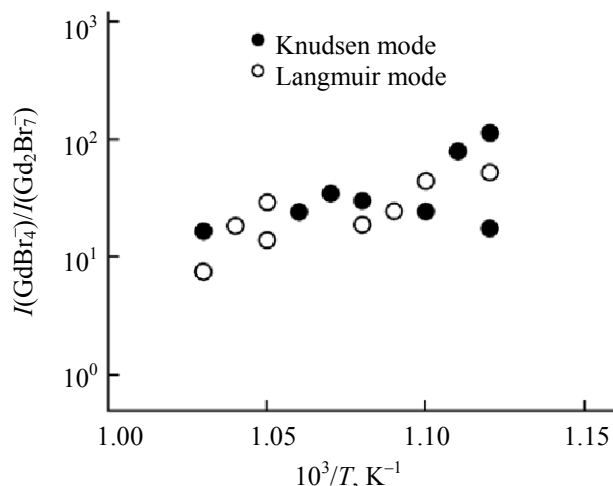


**Fig. 3.** Temperature dependence of relative partial ionization cross sections  $\Phi$  in Knudsen and Langmuir sublimation modes (using the  $\text{TbBr}_3$  molecule as an example).

ions (Table 5) were determined on the basis of the obtained enthalpies of reactions (4) and (5) [Eq. (3)] and also of the enthalpies of formation  $\Delta_f H^0(298 \text{ K})$  of gaseous molecules and ions in gas state  $\{-538 \pm 15$  ( $\text{LuBr}_3$ ),  $-584 \pm 10$  ( $\text{LaBr}_3$ ),  $-1085 \pm 23$  ( $\text{LuBr}_4^-$ ), and  $-1105 \pm 14$  ( $\text{LaBr}_4^-$ ) [2] $\}$  and in crystals  $\{-838.2 \pm 2.0$  ( $\text{GdBr}_3$ ),  $-843.5 \pm 3.0 \text{ kJ mol}^{-1}$  ( $\text{TbBr}_3$ ) [18] $\}$ .

**Measurements in Langmuir mode.** The mass spectra of molecular sublimation, except for the  $\text{Tb}_3\text{Br}_8^+$  ion, which was not recorded in this mode, are identical in qualitative composition to the corresponding mass spectra of the vapor above the studied tribromides observed in Knudsen mode. At the same time essential differences both in relative intensities of ionic currents and in their temperature dependences are observed. The aforesaid is readily illustrated by Fig. 3, where temperature dependences of relative partial ionization cross sections  $\Phi$  (ratio of the current of ions of a specified type to a total current of all ions formed from a given molecule) for single-charged ions are presented. We have noted an analogous effect also for others tribromides [1–6]. In our opinion its nature is connected with essential polarization of adsorbed molecules in the field of the surface charge of the ionic crystal resulted in an excess “superthermal” vibration-rotation excitation of molecules sublimated from a crystal open surface [2].

Activation energies of sublimation of crystals of the studied tribromides in the form of monomeric and dimeric molecules and  $\text{LnBr}_4^-$  and  $\text{Ln}_2\text{Br}_7^-$  ions were determined for an average experimental temperature



**Fig. 4.** Temperature dependence of the ratio of intensities of ionic currents  $I(\text{GdBr}_4^-)/I(\text{Gd}_2\text{Br}_7^-)$  in Knudsen and Langmuir sublimation modes.

from slopes of temperature dependences of ionic currents  $\log [\Sigma I_i T / (a_i \gamma_i)] - 1/T$  ( $i$ :  $\text{Ln}^+$ ,  $\text{LnBr}^+$ ,  $\text{LnBr}_2^+$ ,  $\text{LnBr}_3^+$ ,  $\text{Ln}^{++}$ ,  $\text{LnBr}^{++}$ , and  $\text{LnBr}_2^{++}$  are monomers;  $i$ :  $\text{Ln}_2\text{Br}_4^+$ ,  $\text{Ln}_2\text{Br}_5^+$  are dimers) and  $\log I_i T^{1/2} - 1/T$  ( $i$ :  $\text{LnBr}_4^-$  and  $\text{Ln}_2\text{Br}_7^-$ ), which are presented in Table 5.

Comparison of sublimation activation energies and enthalpies for the studied tribromides shows that the enthalpies of monomeric molecules  $\text{LnBr}_3$  and  $\text{LnBr}_4^-$  ions are close in values, and within the error limits they can be considered as equal. A similar correspondence is observed also for the corresponding parameters of the sublimation in the form of  $\text{Ln}_2\text{Br}_6$  dimeric molecules and  $\text{Ln}_2\text{Br}_7^-$  ions. Whereas the activation energies and enthalpies of the sublimation in the form of monomeric and dimeric molecules are close to each other, the ratio of dimeric and monomeric molecules has appeared to be higher on the evaporation in Knudsen mode. This experimental fact reflects differences in the sublimation coefficients of dimers  $\alpha_s(\text{Ln}_2\text{Br}_6)$  and monomers  $\alpha_s(\text{LnBr}_3)$ . On the basis of relative intensities of ionic currents measured in two sublimation modes, we have estimated the ratio of partial sublimation coefficients  $\alpha_s(\text{LnBr}_3)/\alpha_s(\text{Ln}_2\text{Br}_6)$  for the studied tribromides at factors 15.7 ( $\text{GdBr}_3$ ) and 2.2 ( $\text{TbBr}_3$ ). We note that of all studied tribromides [1–6] the greatest decrease in the fraction of dimers is observed for  $\text{GdBr}_3$  on passing from Knudsen mode to Langmuir mode.

Assumed reasons of the decrease in the oligomerization degree of molecular flows in Langmuir mode can be a damped surface diffusion of adsorbed

**Table 7.** Input data and results of calculation of electron work function for LnBr<sub>3</sub> crystals

Process	Parameter	Value, kJ mol <sup>-1</sup> <sup>a</sup>	
		GdBr <sub>3</sub>	TbBr <sub>3</sub>
LnBr <sub>4</sub> <sup>-</sup> (in a matrix template of LnBr <sub>3</sub> crystals) = LnBr <sub>4</sub> <sup>-</sup> (gas)	$\Delta_s H_i^0$	273±12	280±8
LnBr <sub>3</sub> (cr.) = LnBr <sub>3</sub> (gas)	$\Delta_s H^0$	281±10	278±10
LnBr <sub>4</sub> <sup>-</sup> (gas) = Br <sup>-</sup> (gas) + LnBr <sub>3</sub> (gas)	$\Delta_r H^0$	307±18	309±26
LnBr <sub>3</sub> (gas) = Ln (gas) + 3Br (gas)	$\Delta_{at} H^0$	1282±12	1279±12
Br (gas) + e <sup>-</sup> = Br <sup>-</sup> (gas)	$A_0$	324.7±0.3 [20]	
$\varphi_e$ , eV		2.6±0.2	2.8±0.2

<sup>a</sup> Presented values refer to the average temperature of the studied ranges: 900 K (GdBr<sub>3</sub>) and 1000 K (TbBr<sub>3</sub>).

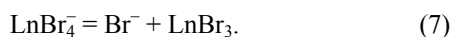
molecules of dimers as compared with monomers owing to their greater polarizability and also a retardation of rotation and distortion of molecular structure in an electric field of a crystal surface charge [2].

A special feature of the ionic sublimation study is the fact that in the studied temperature range (Fig. 4) the ratio of ionic currents  $I(\text{LnBr}_4^-)/I(\text{Ln}_2\text{Br}_7^-)$  is independent of a sublimation mode. This result confirms the assumption [2] about the “diffusionless” mechanism of sublimation of ionic associates.

*Electron work function.* The ion LnBr<sub>4</sub><sup>-</sup> was most intensive in the thermoionic emission mass spectrum. Emission of LnBr<sub>4</sub><sup>-</sup> was observed in rather wide temperature ranges that has allowed us to determine reliably the values of sublimation enthalpies ( $\Delta_s H_i^0$ ) of the studied tribromides in the form of LnBr<sub>4</sub><sup>-</sup> ions and to calculate the electron work function for LnBr<sub>3</sub> crystals by Eq. (6) [19].

$$\varphi_e = \Delta_s H_i^0 - 1/4\Delta_{at} H^0 - 5/4\Delta_s H^0 + A_0 + \Delta_r H^0. \quad (6)$$

Here  $\Delta_{at} H^0$  is the enthalpy of the reaction of LnBr<sub>3</sub> atomization,  $A_0$  is the bromine atom electron affinity, and  $\Delta_r H^0$  is the enthalpy of gas-phase reaction (7).



Input data and results of the  $\varphi_e$  calculation are presented in Table 7. The resulting values of the electron work function are thermodynamically reversible effective parameters related to the average temperature of the studied ranges.

## EXPERIMENTAL

The work was fulfilled on an MI 1201 mass-spectrometer adapted for high-temperature investigations at the energy of ionizing electrons 70 eV. An

energy scale of ionizing electrons was calibrated using the ionization energy of silver atoms and water molecules as standards [20]. The error in appearance energies was estimated at ±0.5 eV for single-charged and ±1 eV for two-charge ions. The detailed description of the installation and experimental techniques is given in [1].

Samples under study of 99.99% purity were evaporated from a molybdenum cell with the ratio of a sectional area to the effusion orifice area ( $d$  0.6 mm) of about 400. In Langmuir mode GdBr<sub>3</sub> and TbBr<sub>3</sub> single crystals were fixed in a molybdenum holder; the (001) face of a crystal (3×3 mm) obtained by spalling directly before placing of an evaporator in the mass-spectrometer was exposed for sublimation.

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