

STRUCTURE OF MATTER AND QUANTUM CHEMISTRY

The Thermodynamic Stability of the LaBr_4^- Ion

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Abstract—The thermodynamic stability of the LaBr_4^- anion was for the first time studied by high-temperature mass spectrometry and nonempirical quantum-chemical methods. The experimental and theoretical enthalpies of the reaction



were $\Delta_f H^\circ(298.15 \text{ K}) = 302 \pm 14$ and 303 kJ/mol , respectively. The value $\Delta_f H^\circ(\text{LaBr}_4^-, \text{g}, 298.15 \text{ K}) = -1105 \pm 14 \text{ kJ/mol}$ was recommended as the enthalpy of formation of the LaBr_4^- anion.

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INTRODUCTION

The method of ion-molecular equilibria as a variant of high-temperature mass spectrometry was developed in the 1970–1980s [1–3] and showed itself as one of the most effective methods for determining the thermochemical properties of positive and negative ions in the gas phase [4–6]. It is based on measuring ion currents formed at high temperatures inside a Knudsen effusion cell containing the system or pure compound to be studied.

The determination of the thermodynamic parameters of ions is based on measurements of ion-molecular reaction equilibrium constants. One of the ions participating in the reaction plays the role of a “reference,” whose enthalpy of formation was determined reliably. The selection of the reference is most important for the method of ion-molecular reactions, and much methodological work has been directed toward its solution. In particular, the use of the most attractive references, such as atomic alkali metal M^+ or halogen X^- ions, which are effectively produced in thermal ionization, was found to be problematic. Studies showed [7] that the measured currents of these ions were as a rule total signals of ions formed under equilibrium conditions inside effusion cells and on their outside surfaces. Outside surface ions form an undesirable background. Instrumental methods used to eliminate it, such as the selection of the corresponding focusing conditions in an ion source [8] and/or ionic beam collimation [9] cannot guarantee a solution to this problem, although they have been continuously perfected [10]. New approaches are therefore required.

We have been performing systematic studies of the thermochemical properties of negative lanthanide

halide ions in the gas phase [11]. In this work, we suggest a new experimental approach for the example of lanthanum tribromide. It is based on a comparison of measurements of the thermal emission of ions formed in saturated vapor over LaBr_3 inside a Knudsen effusion cell and on an open surface of a single crystal. Using this approach, we for the first time determined the enthalpy of formation of the LaBr_4^- ion experimentally. The reliability of the results was substantiated by quantum-chemical calculations.

We recommend LaBr_4^- as a reference for the determination of the thermodynamic parameters of negative ions of the other lanthanide halides in studying exchange ion-molecular reactions in $\text{LnHal}_3\text{--LaBr}_3$ binary systems.

EXPERIMENTAL

We used an MI1201 mass spectrometer ($\angle 90^\circ$, radius of curvature 200 mm) modified for high-temperature thermodynamic studies. Experiments were performed as follows. The substance to be studied was loaded into an effusion cell in the form of a powder or, if a single crystal was used, fixed in a cylindrical holder. Ions of thermal origin formed inside the cell or on the open surface of the single crystal were drawn off by a low electric field ($10^4\text{--}10^5 \text{ V/m}$) created between the cell or holder and a collimating electrode and focused into a narrow beam by a system of electrostatic lenses. A high electric potential (3 kV) determining the energy of ions at the exit of the ion source was applied to the cell or holder. The deflecting capacitor mounted at the exit of the ion source allowed conditions to be selected

Table 1. Experimental data and calculated enthalpies of reaction (I)

<i>T</i> , K	$-\ln K_p$	$-\Delta_r \Phi^\circ(T)$, J/(mol K)	$-\Delta_r H^\circ(0 \text{ K})$, kJ/mol
Effusion cell conditions			
1007	7.82	103.3	38.6
1010	7.85	103.2	38.3
1016	7.94	103.1	37.7
1018	7.83	103.1	38.6
1025	7.59	102.9	40.8
1030	8.09	102.8	36.6
1032	7.79	102.8	39.2
1035	7.91	102.8	38.3
1038	8.32	102.7	34.8
1046	7.90	102.5	38.5
1051	8.40	102.4	34.2
	Mean	37.8 (35.2)	
<i>1076</i>	<i>8.40</i>	<i>101.3</i>	<i>33.8</i>
<i>1094</i>	<i>7.49</i>	<i>100.1</i>	<i>41.4</i>
<i>1113</i>	<i>6.96</i>	<i>98.8</i>	<i>45.6</i>
<i>1125</i>	<i>6.74</i>	<i>98.1</i>	<i>47.3</i>
<i>1135</i>	<i>6.19</i>	<i>97.5</i>	<i>52.2</i>
<i>1157</i>	<i>5.09</i>	<i>96.1</i>	<i>62.2</i>
Open surface conditions			
1027	9.58	102.9	23.9
1043	9.82	102.6	21.9
1048	10.34	102.5	17.3
	Mean	21.0 ± 10 (18.4 ± 10)	

Note: Data obtained above the melting point ($T_m = 1061 \text{ K}$) are typeset in italics; values preceded by \pm are total errors including systematic errors in thermodynamic functions and statistical errors corresponding to a 95% confidence interval; the mean $\Delta_r H^\circ(298.15 \text{ K})$ values are parenthesized.

for recording ions drawn off predominantly from the inside cell cavity. After the passage through a magnetic filter, ions of the required mass were directed to a recording system operated under direct current conditions. This system was a combination of a secondary electron multiplier and an electrometric amplifier. The sensitivity of the recording scheme for direct current measurements was 10^{-17} A .

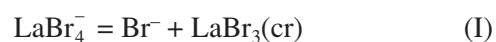
We studied lanthanum tribromide powders of purity 99.99% and LaBr_3 single crystals ($3 \times 3 \times 10 \text{ mm}$) grown from these powders by the vertical Bridgman method; the (001) single crystal face ($3 \times 3 \text{ mm}$) was exposed, it was cleaved directly before mounting the vaporizer in the mass spectrometer. Prior to measurements, the samples loaded from evacuated ampules at atmospheric pressure were dehydrated in a $\sim 10^{-1} \text{ Pa}$

vacuum directly in the mass spectrometer at $\sim 150^\circ\text{C}$ for several hours to remove adsorbed moisture.

RESULTS AND DISCUSSION

We recorded the Br^- , LaBr_4^- , and La_2Br_7^- negative ions in studies of the ionic sublimation of lanthanum tribromide from the effusion cell and open single crystal surface at 1007–1157 K. Importantly, the signal of Br^- atomic ions was substantially lower when vaporization was performed from the open surface, the signals of polyatomic ions being comparable in the two regimes.

To determine the thermodynamic stability of the LaBr_4^- anion, we studied the heterophase reaction



in both regimes. We used the equation

$$p = \frac{\kappa I_i T^{1/2} M^{1/2}}{\gamma a_i}, \quad (1)$$

where p and I_i are the partial pressure and the experimental ion current value of the i th isotope of ions of the given type, respectively; κ is the sensitivity constant of the mass spectrometer; T is the temperature of the cell; M is the molecular weight; γ is the ion–electron conversion coefficient (it was assumed that $\gamma \sim M^{-1/2}$); and a_i is the natural abundance of the i th isotope. The reaction (I) equilibrium constant is then given by the equation

$$K_p(I) = \frac{p(\text{Br}^-)}{p(\text{LaBr}_4^-)} \quad (2)$$

$$= \frac{I(\text{Br}^-)}{I(\text{LaBr}_4^-)} \left[\frac{M(\text{Br}^-)}{M(\text{LaBr}_4^-)} \right] \left[\frac{a(\text{LaBr}_4^-)}{a(\text{Br}^-)} \right].$$

The reaction equilibrium constants measured at various temperatures and the enthalpies of the reaction calculated using the third law of thermodynamics are listed in Table 1. The thermodynamic functions of LaBr_3 in the condensed state and the Br^- ion in the gas phase necessary for the calculations were taken from [12] and [13], respectively. The thermodynamic functions of LaBr_4^- in the ideal gas state were calculated in the rigid rotator–harmonic oscillator approximation from the molecular constants obtained in this work (see below). The reduced Gibbs energies (J/(mol K)) and enthalpy functions (J/mol) used in the calculations were approximated by the polynomials [13]

$$\Phi^\circ(T) = -(G^\circ(T) - H^\circ(0))/T = f_0 + f \ln X \quad (3)$$

$$+ f_{-2}/X^{-2} + f_{-1}/X^{-1} + f_1 X + f_2 X^2 + f_3 X^3,$$

Table 2. Parameters of polynomials (3) and (4)

Compound	f_0	f	f_{-2}	f_{-1}	f_1	f_2	f_3
LaBr ₃ (cr)	106.729	1.135	0.013	-2.004	1703.372	-6351.800	13150.268
LaBr ₄ ⁻	716.814	107.119	-8.778	0.553	12.887	-38.922	57.311

Note: The electronic contribution to the thermodynamic functions of the LaBr₄⁻ ion in the gas phase in the rigid rotator-harmonic oscillator approximation was set equal to zero (the statistical weight of the ground electronic state of the La³⁺ ion is 1). The contribution of excited electronic states to the thermodynamic functions was not included. Errors in the Gibbs energies were taken to be equal to ± 3 and ± 14 J/(mol K) for LaBr₃(cr) and LaBr₄⁻, respectively, at $T = 1000$ K.

$$H^\circ(T) - H^\circ(0) = T(f - 2f_{-2}/X^2 - f_{-1}/X + f_1X + 2f_2X^2 + 3f_3X^3), \quad (4)$$

where $X = T/10^4$. The coefficients of polynomials (3) and (4) are listed in Table 2. We see from Table 1 that the enthalpies of reaction (I) obtained under equilibrium conditions and under the conditions of vaporization from the open surface of the single crystal differ from each other.

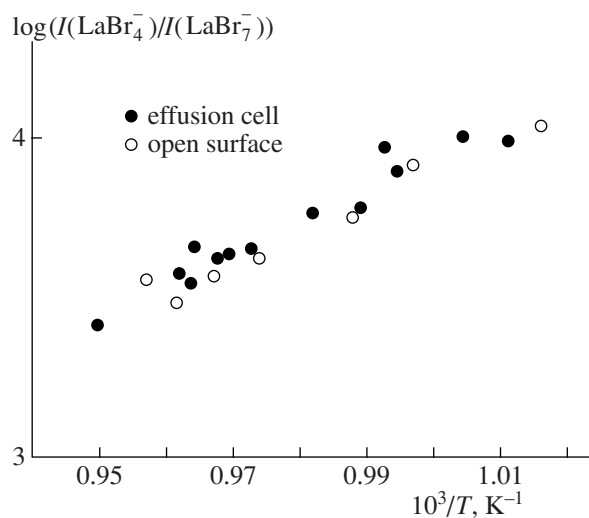
The largest differences were obtained for measurements under effusion cell conditions performed at temperatures higher than the melting point of lanthanum tribromide ($T_m = 1061$ K [12]). We then observe a systematic trend in the $\Delta_r H^\circ$ (0 K) values. These differences, in our view, have a quite obvious explanation. As was mentioned above, measurements of the equilibrium concentrations of halogen ions are complicated by a contribution of the emission of these ions from the outside cell surface. Microamounts of the substance studied appear on a cell lid in the form of a thin film because of the surface diffusion of metal halides from internal cell cavities onto their surfaces directly through effusion orifices. The effect becomes especially noticeable if the substance in the cell is in the molten state. This is clearly seen as a systematic trend in the $\Delta_r H^\circ$ (I) values determined under effusion cell conditions at temperatures above the melting point. Such changes in $\Delta_r H^\circ$ (I) are a consequence of an increase in the contribution of surface ions to the measured Br⁻ ion signal.

Open surface vaporization conditions provide an additional methodological advantage if procedures for the elimination of "foreign" bromide anions (defocusing conditions of drawing off ions and ionic beam collimation) are used. The larger surface area of the crystal compared with the effusion orifice area provides actually ideal collimation and completely eliminates surface ion signals. The question, however, arises of the establishment of ion-molecular equilibrium, in particular, in reaction (I), on the open crystal surface.

First, note that the use of the procedure with polarity reversal of the electric field drawing ions off [14] showed that there was no accumulation of Br⁻ ions on the surface during the time of reversal. This, in particular, eliminates dislocations that emerge on the surface of the crystal [15] as sources of bromine anions. In all

probability, adsorbed Br⁻ ions, like adsorbed LaBr₃ molecules, are produced directly on the surface in detachment from vaporization step kinks. Suppose that the LaBr₄⁻ and La₂Br₇⁻ ions (homologues of the La_{*n*}Br_{3*n*+1}⁻ series) are formed as a result of the successive addition of LaBr₃ adsorbed molecules to the Br⁻ adsorbed ion. Important evidence for the establishment of equilibrium is then equal $I(\text{LaBr}_4^-)/I(\text{La}_2\text{Br}_7^-)$ ion current ratios under equilibrium and free sublimation conditions. The temperature dependence of this ratio is shown in the figure. We see that the $I(\text{LaBr}_4^-)/I(\text{La}_2\text{Br}_7^-)$ value virtually does not change in passing from the effusion cell to open surface conditions (to within measurement errors).}

Another convincing proof of the establishment of equilibrium can be obtained from a comparison of the thermodynamic stability of LaBr₄⁻ in the gas phase obtained experimentally and calculated by modern quantum-chemical methods.



Dependence of the ratio between ion currents $I(\text{LaBr}_4^-)/I(\text{La}_2\text{Br}_7^-)$ on inverse temperature under effusion cell and open surface conditions.

Table 3. Internuclear distances ($R_e(\text{La}-\text{Br})$, Å), vibrational frequencies (ω_i , cm^{-1}) and band intensities (A_i , km/mol , parenthesized) in the IR spectra of the LaBr_3 molecule and LaBr_4^- anion

Source	Method	Structure	R_e	ω_1	ω_2	ω_3	ω_4
LaBr_4^-							
Our data [28]	DFT/B3LYP	T_d	2.845	165	39	196(196)	50(7)
	SDTQ-MP4	T_d	2.825	172	40	208(220)	49(9)
	CISD + Q	T_d	2.833	172	40	206(238)	51(12)
LaBr_3							
Our data	DFT/B3LYP	D_{3h}	2.765	187	$8i$	233(163)	44(3)
		C_{3v}	2.764	187(0.5)	10(20)	233(162)	44(3)
[27]			<i>119.5</i>				
		C_{3v}	2.689 ± 0.020	207 ± 10	$30 \pm 10^*$	$232 \pm 5^*$	57 ± 10
			<i>118.0 ± 2.0</i>				

Note: Frequencies are given according to the following vibrational representations: LaBr_4^- , T_d symmetry, $\Gamma_{\text{vib}} = a_1 + e + 2t_2$; LaBr_3 , D_{3h} , $\Gamma_{\text{vib}} = a'_1 + a''_2 + 2e'$; and LaBr_3 , C_{3v} , $\Gamma_{\text{vib}} = 2a_1 + 2e$; $\alpha_e(\text{BrLaBr})$ valence angles are given in degrees in italics; experimental vibrational frequencies are asterisked (see review [27] and the references therein).

Theoretical Study

Theoretically, the stability of LaBr_4^- can be analyzed by calculating the enthalpy of the reaction that determines the affinity of the LaBr_3 molecule for the bromine anion,



The nonempirical calculations of the LaBr_4^- ion and LaBr_3 molecule were performed using density functional theory at the DFT/B3LYP [16–18] level implemented in the PC GAMESS version [19] of the GAMESS package [20]. The atomic cores described using relativistic effective potentials [21–23] included the $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ (Br, La) and $4s^2 4p^6 4d^{10}$ (La) orbitals. The electrons directly included into calculations were described by the $(7s6p5d/5s4p3d)$ (La [22]) and $(14s10p2d1f/3s3p2d1f)$ (Br [24]) valence triple-zeta (pVTZ) basis sets augmented by polarization f type functions on La ($5f/3f$) [25] and one-exponential sets of diffuse s , p , d , and f functions on Br [24]. The pseudopotential and basis set parameters were taken from database [26].

Calculations of the molecular parameters of the LaBr_4^- ion were performed for the tetrahedral configuration of nuclei, T_d symmetry. For LaBr_3 , two geometric configurations were considered, planar of D_{3h} symmetry and pyramidal of C_{3v} symmetry. The optimization of geometric parameters and calculations of force constants and normal vibration frequencies were performed using the methods implemented in the GAMESS package.

The calculated molecular parameters of the LaBr_3 molecule and LaBr_4^- anion are listed in Table 3.

According to the data obtained, a pyramidal structure (C_{3v} symmetry) corresponds to the potential energy surface minimum of the LaBr_3 molecule. A planar configuration of D_{3h} symmetry corresponds to a first-order saddle point of the potential energy surface. It follows that the relative energy of the planar structure determines the height of the barrier to inversion of the LaBr_3 molecule. According to our data, the barrier is fairly low, of 9 J/mol.

The structure of the LaBr_3 molecule has been studied extensively during several decades. The results obtained, both theoretical and experimental, were analyzed in detail in [27]. A nonempirical study of the structure and energy stability of the LaBr_4^- ion by the SDTQ-MP4 and CISD + Q methods was performed in [28]. The geometric parameters and normal vibration frequencies of the LaBr_3 molecule and LaBr_4^- ion calculated in this work were close to those reported in [27] and [28], respectively (see Table 3).

In addition to reaction (II), we calculated the energies of the heterolytic decomposition of the LaBr_4^- ion and LaBr_3 molecule,



These calculations were mainly performed to determine the errors in dissociation energies ($\Delta_r E$), which appear because of the neglect of basis set superposition errors in calculations of the total energies of the products of reactions (II)–(IV). The basis set superposition errors for reactions (III) and (IV) were calculated using the well-known counterpoise method. For (II), the procedure recommended in [28] was used. The authors of

[28] suggested that the basis set superposition error could be found by calculating $\Delta_r E$ (II) using the Hess cycle and the $\Delta_r E$ (III) and $\Delta_r E$ (IV) values corrected by the counterpoise method. The result should then be compared with the value obtained directly from the total energies of reaction (II) products and initial substances.

The energies of reactions (II)–(IV) listed in Table 4 show that the inclusion of basis set superposition errors changes these energies very insignificantly (by ~ 1 kJ/mol). This is evidence that the basis sets used were fairly complete. The use of more extended basis sets in our work is likely the main reason for the discrepancies between the theoretical parameter values obtained in this work and [28] (see Tables 3 and 4).

Table 4 contains the enthalpy of reaction (II) at $T = 0$ K. Recalculation to $T = 298.15$ K insignificantly (by 0.1 kJ/mol) increased the enthalpy of the reaction and gave $\Delta_r H^\circ(298.15 \text{ K}) = 303$ kJ/mol. The $H^\circ(T) - H^\circ(0)$ functions used in the recalculation were obtained in the rigid rotator–harmonic oscillator approximation. Note that this approximation is not absolutely valid for LaBr_3 molecules, because the literature data and the data obtained in this work show that the inversion potential of LaBr_3 is anharmonic to a substantial extent. This problem was considered in detail in [29] for the example of the related LaF_3 and LaCl_3 molecules. It was shown in [29] that the $[H^\circ(T) - H^\circ(0)]$ functions calculated in the rigid rotator–harmonic oscillator approximation and by the direct summation of vibrational energy levels obtained by solving the Schrödinger vibrational equation differ by 0.6 kJ/mol at $T = 298.15$ K. At $T = 1000$ K, the discrepancy increases to ~ 2 kJ/mol [29]. Similar rigid rotator–harmonic oscillator approximation errors can likely be expected for the LaBr_3 molecule.

A Comparison of Experimental and Theoretical Results

Combining the enthalpy of reaction (I) obtained under open surface conditions with the enthalpy of sublimation of lanthanum tribromide $\Delta_s H^\circ(298.15 \text{ K}) = 320 \pm 10$ kJ/mol determined in a separate experiment yields the enthalpy of reaction (2) $\Delta_r H^\circ(298.15 \text{ K}) = 302 \pm 10$ kJ/mol. This value closely agrees with the enthalpy calculated theoretically, 303 kJ/mol. This substantiates the establishment of equilibrium in reaction (I) on the surface of the single crystal. A similar value obtained from effusion cell measurements, 285 kJ/mol (we used the $\Delta_r H^\circ(\text{I}) = -37.8$ kJ/mol value for measurements below the melting point of lanthanum tribromide), includes a systematic error related to the contribution of surface ions to the measured $I(\text{Br}^-)$ current values (see above).

Table 4. Energies ($\Delta_r E$) and enthalpies ($\Delta_r H^\circ$) of reactions and corrections for zero point energies ($\Delta_r ZPE$)

Source	Reaction	$\Delta_r E$	$\Delta_r E_{\text{BSSE}}$	$-\Delta_r ZPE$	$\Delta_r H^\circ(0)$
LaBr_4^-					
Our data	(II)	305	304	1	303
	(III)	4087	4086	6	4080
[28]	(II)	326	320	1	319
LaBr_3					
Our data	(IV)	3782	3781	4	3777

Note: All values are in kJ/mol; $\Delta_r E$ denotes dissociation energies uncorrected for basis set superposition errors, and $\Delta_r E_{\text{BSSE}}$ is dissociation energy calculated taking into account basis set superposition errors. Calculations of the energy characteristics of reactions with the participation of the LaBr_3 molecule were performed using the data on the configuration of C_{3v} symmetry.

The Enthalpy of Formation of the LaBr_4^- Anion

Using the literature data on the enthalpies of formation of lanthanum tribromide in the crystalline state ($\Delta_f H^\circ(\text{LaBr}_3, \text{cr}, 298.15 \text{ K}) = -904.4 \pm 1.5$ [30]) and $\Delta_r H^\circ(\text{Br}^-, \text{g}, 298.15 \text{ K}) = -219.037 \pm 0.3$ kJ/mol [13]), we obtain the enthalpy of formation of the LaBr_4^- anion $\Delta_f H^\circ(\text{LaBr}_4^-, \text{g}, 298.15 \text{ K}) = -1105 \pm 14$ kJ/mol.

CONCLUSIONS

To summarize, our complex experimental and theoretical study allowed the enthalpy of the detachment of the bromine anion from the LaBr_4^- anion to be determined with a high degree of reliability, $\Delta_r H^\circ(298.15 \text{ K}) = 302 \pm 10$ kJ/mol. We showed for the example of lanthanum tribromide that studies of ionic sublimation from single crystals are a new promising method for the determination of the thermochemical properties of negative ions. The enthalpy of formation of the lanthanum tetrabromide ion $\Delta_f H^\circ(\text{LaBr}_4^-, \text{g}, 298.15 \text{ K}) = -1105 \pm 14$ kJ/mol can be recommended as a reference value for mass spectrometric studies of the thermochemical properties of lanthanide halide negative ions.

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