

CHEMICAL THERMODYNAMICS  
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## Formation Enthalpies of Molecules and Negative Ions of Ytterbium Bromides

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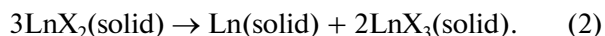
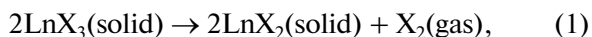
**Abstract**—A procedure for determining the formation enthalpies of  $\text{LnX}_n$  ( $n = 1-3$ ) molecules of thermally unstable lanthanide di- and trihalides that is based on measuring the equilibrium constants of reactions in  $\text{Ln-X}$  systems of various content and solving a system of thermochemical equations is suggested. The procedure is used to determine the enthalpies of formation  $\Delta_f H_{298}^\circ$  of molecules and negative ions found in the vapors of ytterbium bromides:  $\text{YbBr}$  ( $20 \pm 3$ ),  $\text{YbBr}_2$  ( $-135 \pm 10$ ),  $\text{YbBr}_3$  ( $-233 \pm 12$ ),  $\text{YbBr}_3^-$  ( $-615 \pm 31$ ), and  $\text{YbBr}_4^-$  ( $-766 \pm 23$ ) kJ/mol.

**Keywords:** ytterbium bromide, ions, formation enthalpy of molecules, lanthanides, equilibrium constants.

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### INTRODUCTION

The thermochemical properties of lanthanide halides have recently been described quite exhaustively [1–4]. An exception is the halides of valent-unstable *f*-elements (Eu, Yb, Sm), for which there are no reliable experimental values in the literature for the enthalpies of the formation of molecules in the gas phase, due to the complicated nature of the decomposition and disproportionation reactions that take place at high temperatures:



We recently demonstrated in [5] that the saturated vapor over ytterbium bromides contains Yb atoms and molecules  $\text{YbBr}$ ,  $\text{YbBr}_2$ , and  $\text{YbBr}_3$ . In addition, regardless to the initial composition of the system under study,  $\text{YbBr}_2$  or  $\text{YbBr}_3$ , the vaporization at the initial steps is incongruent. The complex composition of vapor and the uncertainty of the condensed phase [6, 7] do not allow us to use general approaches to determining the sublimation enthalpies and enthalpies of formation of individual compounds.

In this work, we propose a procedure for determining the enthalpies of formation of the molecules  $\text{YbBr}$ ,  $\text{YbBr}_2$ , and  $\text{YbBr}_3$  that is based on the experimental results obtained in [5] and on solving a system of thermochemical equations. We also study the thermal emission of negative ions for the first time and deter-

mine their thermodynamic characteristics using ion-molecular equilibria [8, 9].

### EXPERIMENTAL

Each experiment was performed on an MI 1201 mass spectrometer ( $\angle 90^\circ$ ; radius of curvature, 200 mm), re-equipped with a Knudsen cell (graphite and molybdenum) for high-temperature effusion measurements with a coaxial distribution of molecular and ionic beams. The structure of the device provided an opportunity to study the molecular and ionic components of vapor in one experiment. The molecular composition of the saturated vapor was determined by conventional mass spectrometry, using ionization with electrons. The ions of a thermal nature formed inside the cell were stretched by a small electric field (with an intensity of  $10^4$  to  $10^5 \text{ V m}^{-1}$ ) formed between the cell and the electrode collimator and were focused into a narrow beam by a system of electrostatic lenses. A detailed description of the instrument and the measurement procedure is given in [10].

### RESULTS AND DISCUSSION

**Enthalpies of the formation of molecules.** Reactions I–III were considered in determining the enthalpies of formation of the  $\text{YbBr}$ ,  $\text{YbBr}_2$ , and  $\text{YbBr}_3$  molecules present in the vapor over the Yb–Br system [5] (Table 1). The equilibrium constants of these reactions

**Table 1.** Equilibrium constants and enthalpies of reactions  $\text{YbBr}_3 = \text{YbBr}_2 + 0.5\text{Br}_2$  (I),  $1.5\text{YbBr}_2 = \text{YbBr}_3 + 0.5\text{Yb}$  (II),  $\text{YbBr}_3 + \text{YbBr} = 2\text{YbBr}_2$  (III),  $\text{YbBr}_2 + \text{LaBr}_4^- = \text{LaBr}_3 + \text{YbBr}_3^-$  (IV), and  $\text{YbBr}_3 + \text{LaBr}_4^- = \text{LaBr}_3 + \text{YbBr}_4^-$  (V)

<i>T</i> , K	$-\ln K_p^\circ$	<i>T</i> , K	$-\ln K_p^\circ$	<i>T</i> , K	$\ln K_p^\circ$	<i>T</i> , K	$-\ln K_p^\circ$	<i>T</i> , K	$\ln K_p^\circ$
(I)		(II)		(III)		(IV)		(V)	
846	9.98	1285	6.17	1285	5.41	1108	2.99	1108	2.55
849	10.19	1300	5.76	1300	5.44	1154	3.32	1154	2.06
894	8.88	1296	6.35	1126	6.08	1199	2.77	1199	0.83
937	8.26	1179	6.6	1196	5.77	1221	3.4	1221	0.99
997	7.91	1175	6.82	1208	5.67				
1000	7.92	1197	7.25	1143	5.89				
971	7.58	1221	6.55	1181	5.85				
977	7.42	1263	6.81	1138	6.06				
		1143	6.75						
$\Delta_r H_{298}^\circ$ , kJ/mol									
109 ± 14		54 ± 25		-50 ± 10		—		—	
114 ± 16		45 ± 19		-56 ± 23		42 ± 24		-11 ± 8	

Note: The error in the values of enthalpies of reactions calculated by the II law (upper row) is the standard deviation; in the values calculated by the III law (lower row), it is the total error. The error in the enthalpy of reaction (V) was calculated with allowance for the mutual compensation of the errors in the functions of the components in the right and left sides of the reaction.

**Table 2.** Thermodynamic functions of I,  $-\{G^\circ(T) - H^\circ(298.15)\}/T$ , J/(mol K), and II,  $H^\circ(T) - H^\circ(298.15)$ , kJ/mol

<i>T</i> , K	I	II	I	II	I	II	I	II
	YbBr		YbBr <sub>2</sub>		YbBr <sub>3</sub>		YbBr <sub>4</sub> <sup>-</sup>	
298.15	270.6	0.0	337.7	0.0	400.4	0.0	456.5	0.0
500	274.3	7.5	343.3	11.6	408.7	16.5	467.5	21.4
700	280.4	14.9	352.7	23.1	422.2	32.9	485.2	42.9
900	286.5	22.4	362.0	34.7	435.5	49.5	502.6	64.4
1100	291.9	29.9	370.3	46.3	447.4	66.1	518.1	86.0
1300	296.5	37.3	377.4	57.9	457.6	82.6	531.5	107.5
1500	300.5	44.8	383.5	69.5	466.6	99.3	543.2	129.1

$K_p^\circ$  were calculated on the basis of the measured partial pressures of the components of saturated vapor [5]. From the methodological point of view, it is important to note that these reactions can be studied only for various compositions of the Yb–Br system [5], particularly at different steps of the vaporization of the YbBr<sub>3</sub> preparation, while a change in the qualitative and quantitative composition of the vapor takes place over time, due to the incongruent vaporization.

The enthalpies  $\Delta_r H_{298}^\circ$  of reactions I–III were determined using the procedures of the second and third law of thermodynamics (Table 1). The thermodynamic functions  $-\{G^\circ(T) - H^\circ(298.15 \text{ K})\}/T$  and  $H^\circ(T) - H^\circ(298.15 \text{ K})$ , required for the calculations were narrowed to an approximation of a rigid rotator–

harmonical oscillator for the YbBr and YbBr<sub>3</sub> molecules (Table 2). The molecular constants used in our calculations were taken from [11–13]. The statistical weight of the main electron state of the YbBr and YbBr<sub>3</sub> molecules corresponded to the statistical weight of the main electron state of Yb<sup>+</sup> and Yb<sup>3+</sup> ions [14]. The functions for the YbBr<sub>2</sub> molecules were estimated by the comparative method, based on the data from [15] for YbCl<sub>2</sub> and YbCl<sub>3</sub> (Table 2). The errors in the functions of Gibbs energy were estimated by the procedure proposed in [16] and corresponded to ±3 (YbBr), ±10 (YbBr<sub>2</sub>), and ±12 (YbBr<sub>3</sub>) J/(mol K).

As follows from Table 1,  $\Delta_r H_{298}^\circ$  as calculated by the laws of II and III, agree within the range of error. The

**Table 3.** Formation enthalpies ( $\Delta_f H^\circ$ , 298.15 K), kJ/mol

Obtained data		Employed data		Reference
YbBr	$20 \pm 3$	Yb	$152.5 \pm 0.5$	[16]
YbBr <sub>2</sub>	$-135 \pm 10$	Br <sub>2</sub>	$30.91 \pm 0.11$	[16]
YbBr <sub>3</sub>	$-233 \pm 12$	Br <sup>-</sup>	$-219.03 \pm 0.23$	[16]
YbBr <sub>3</sub> <sup>-</sup>	$-615 \pm 31$	LaBr <sub>3</sub>	$-584 \pm 10$	[20, 19]
YbBr <sub>4</sub> <sup>-</sup>	$-766 \pm 23$	LaBr <sub>4</sub> <sup>-</sup>	$-1105 \pm 14$	[21]

values obtained by the III law were used in all subsequent calculations.

A system of thermochemical equations was solved to determine the enthalpies of formation for the YbBr<sub>3</sub>, YbBr<sub>2</sub>, and YbBr molecules:

$$\Delta_f H_{298}^\circ(\text{I}) = \Delta_f H_{298}^\circ(\text{YbBr}_2) + 0.5\Delta_f H_{298}^\circ(\text{Br}_2) - \Delta_f H_{298}^\circ(\text{YbBr}_3), \quad (3)$$

$$\Delta_f H_{298}^\circ(\text{II}) = \Delta_f H_{298}^\circ(\text{YbBr}_3) + 0.5\Delta_f H_{298}^\circ(\text{Yb}) - 1.5\Delta_f H_{298}^\circ(\text{YbBr}_2), \quad (4)$$

$$\Delta_f H_{298}^\circ(\text{III}) = 2\Delta_f H_{298}^\circ(\text{YbBr}_2) - \Delta_f H_{298}^\circ(\text{YbBr}_3) - \Delta_f H_{298}^\circ(\text{YbBr}), \quad (5)$$

which correspond to reactions I–III (Table 1). All of the values used in and obtained with our calculations are given in Table 3. As follows from the solution for this system, the errors in the enthalpies of formation of YbBr<sub>3</sub>, YbBr<sub>2</sub>, and YbBr are determined only by the errors of their thermodynamic functions.

A comparison of the experimental enthalpies of formation of YbBr<sub>2</sub> and YbBr<sub>3</sub> with the results from quantum–chemical calculations in [17] shows their satisfactory agreement. In particular, the energy of the atomization of ytterbium di- and tribromides, calculated in the highest approximation CISD + Q, yield values of  $-135.6$  (YbBr<sub>2</sub>) and  $-257.9$  (YbBr<sub>3</sub>) kJ/mol when recalculated for the enthalpies of formation.

The enthalpy of formation of ytterbium monobromide was experimentally determined for the first time. The value of the atomization energy of YbBr calculated on its basis corresponds to a reduction in this value in a series of ytterbium monohalides:  $489 \pm 2$  (YbF) [18],  $364 \pm 2$  (YbCl) [18], and  $244 \pm 3$  (YbBr) kJ/mol.

The sublimation enthalpy of ytterbium tribromide  $559 \pm 13$  kJ/mol was calculated using the enthalpy of formation of YbBr<sub>3</sub> for the condensed phase  $-791.9 \pm 5$  kJ/mol [19] and our own  $\Delta_f H_{298}^\circ(\text{YbBr}_3)$ . The value  $285 \pm 9$  kJ/mol published in [2] was obtained by torsion effusion without an analysis of the vapor phase, and is probably erratic: first, the authors [2] analyzed the temperature dependence of the total vapor pressure, whose composition was complex [5]; second and especially important, the composition of the con-

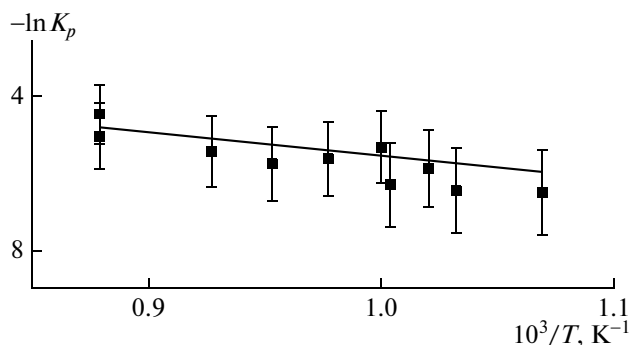
densed phase upon the incongruent vaporization of YbBr<sub>3</sub> becomes uncertain [6, 7]. The obtained value of the sublimation enthalpy substantially exceeds the sublimation enthalpies of other lanthanide tribromides [2–4]. In our opinion, this explains the thermal instability of ytterbium tribromide from the point of view of thermodynamic positions.

**Enthalpies of formation of negative ions.** Ions of YbBr<sub>4</sub><sup>-</sup> were discovered at the stage of the incongruent vaporization of the YbBr<sub>3</sub> preparation in [5] at temperatures near 900 K. Starting from a temperature of 950 K, YbBr<sub>3</sub><sup>-</sup> ions were also recorded in the mass spectrum, the content of which was nearly  $10^{-4}$ . Upon the transition to the stage of congruent vaporization, the concentrations of YbBr<sub>3</sub><sup>-</sup> and YbBr<sub>4</sub><sup>-</sup> ions becomes comparable, as was observed at the stage of the congruent vaporization of the initial preparation of YbBr<sub>2</sub> under study.

Even though there were molecules of ytterbium monobromide in the vapor, none of the stages of experiments with YbBr<sub>3</sub> and YbBr<sub>2</sub> revealed the presence of YbBr<sub>2</sub><sup>-</sup> ions. These ions were not recorded in an additional experiment with the YbBr<sub>2</sub>–Yb system.

The YbBr<sub>2</sub>–LaBr<sub>3</sub> system for which the equilibrium constants of the gas-phase exchange ion–molecular reactions IV and V were obtained (Table 1) and in which LaBr<sub>3</sub> molecules and LaBr<sub>4</sub><sup>-</sup> ions are considered standards [8, 20, 21], was studied to determine the enthalpies of formation of the negative YbBr<sub>3</sub><sup>-</sup> and YbBr<sub>4</sub><sup>-</sup> ions. The enthalpies of these reactions and the enthalpies of the formation of YbBr<sub>3</sub><sup>-</sup> and YbBr<sub>4</sub><sup>-</sup> ions as calculated according to the II law of thermodynamics are given in Tables 1 and 3. The thermodynamic functions of YbBr<sub>4</sub><sup>-</sup> ions (Table 2) were estimated by a comparative method based on the functions LuBr<sub>4</sub><sup>-</sup> [22]. The functions of YbBr<sub>3</sub><sup>-</sup> ions were considered to correspond to the YbBr<sub>3</sub> functions.

The electron affinity of the molecule of ytterbium tribromide  $A_0(\text{YbBr}_3) = 4.0 \pm 0.2$  eV was determined on the basis of the obtained values  $\Delta_f H^\circ(\text{YbBr}_3)$  and  $\Delta_f H^\circ(\text{YbBr}_3^-)$ . It exceeded the electron affinity of atomic bromine  $A_0(\text{Br}) = 3.371 \pm 0.002$  eV [16]. The



Temperature dependence of the equilibrium constant of reaction (6): dots experimental values and line as calculated using the enthalpies of formation for the reactants of (6).

calculated values for the  $\text{YbBr}_2$  and  $\text{YbBr}_3$  molecules' affinity to the bromine anion were  $2.7 \pm 0.2$  and  $3.3 \pm 0.2$  eV, respectively.

The temperature dependence of the equilibrium constant of ion-molecular reaction was analyzed to verify the validity of the thermochemical characteristics:



for the system Yb–Br at the vaporization of ytterbium tribromide as initial preparation. Both the experimental values  $K_p^\circ(6)$  and those calculated using the determined enthalpies of the formation of reactants (6) are given in figure. These values agree with one another within the calculations' range of error. The thermochemical characteristics determined in this work can thus be considered reliable.

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