

CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

Formation Enthalpies of Molecules and Negative Ions of Ytterbium Bromides

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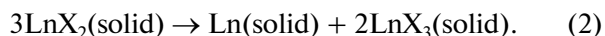
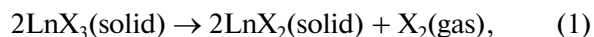
Abstract—A procedure for determining the formation enthalpies of LnX_n ($n = 1-3$) molecules of thermally unstable lanthanide di- and trihalides that is based on measuring the equilibrium constants of reactions in Ln-X systems of various content and solving a system of thermochemical equations is suggested. 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: YbBr (20 ± 3), YbBr_2 (-135 ± 10), YbBr_3 (-233 ± 12), YbBr_3^- (-615 ± 31), and YbBr_4^- (-766 ± 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 YbBr , YbBr_2 , and YbBr_3 . In addition, regardless to the initial composition of the system under study, YbBr_2 or 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 YbBr , YbBr_2 , and 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 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 YbBr , YbBr_2 , and 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 ₂ | | YbBr ₃ | | YbBr ₄ [−] | |
| 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° 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 YbBr₃ 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 YbBr₃ 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 YbBr₃ molecules corresponded to the statistical weight of the main electron state of Yb⁺ and Yb³⁺ ions [14]. The functions for the YbBr₂ molecules were estimated by the comparative method, based on the data from [15] for YbCl₂ and YbCl₃ (Table 2). The errors in the functions of Gibbs energy were estimated by the procedure proposed in [16] and corresponded to ±3 (YbBr), ±10 (YbBr₂), and ±12 (YbBr₃) 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 ± 3 | Yb | 152.5 ± 0.5 | [16] |
| YbBr ₂ | -135 ± 10 | Br ₂ | 30.91 ± 0.11 | [16] |
| YbBr ₃ | -233 ± 12 | Br ⁻ | -219.03 ± 0.23 | [16] |
| YbBr ₃ ⁻ | -615 ± 31 | LaBr ₃ | -584 ± 10 | [20, 19] |
| YbBr ₄ ⁻ | -766 ± 23 | LaBr ₄ ⁻ | -1105 ± 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 YbBr₃, YbBr₂, 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 YbBr₃, YbBr₂, and YbBr are determined only by the errors of their thermodynamic functions.

A comparison of the experimental enthalpies of formation of YbBr₂ and YbBr₃ 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 (YbBr₂) and -257.9 (YbBr₃) 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 ± 2 (YbF) [18], 364 ± 2 (YbCl) [18], and 244 ± 3 (YbBr) kJ/mol.

The sublimation enthalpy of ytterbium tribromide 559 ± 13 kJ/mol was calculated using the enthalpy of formation of YbBr₃ for the condensed phase -791.9 ± 5 kJ/mol [19] and our own $\Delta_f H_{298}^\circ(\text{YbBr}_3)$. The value 285 ± 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-

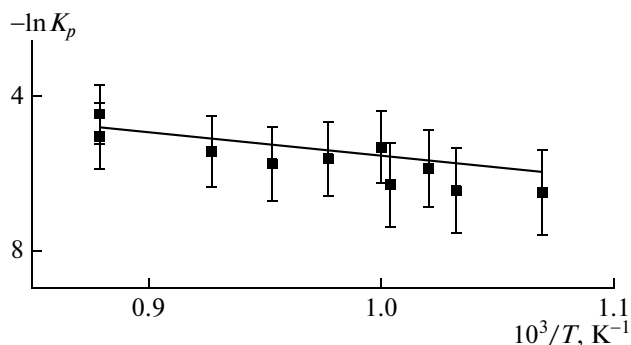
densed phase upon the incongruent vaporization of YbBr₃ becomes uncertain [6, 7]. The obtained value of the sublimation enthalpy substantially exceeds the sublimation enthalpies of other lanthanide tribromides [2–4]. In our opinion, this explains the thermal instability of ytterbium tribromide from the point of view of thermodynamic positions.

Enthalpies of formation of negative ions. Ions of YbBr₄⁻ were discovered at the stage of the incongruent vaporization of the YbBr₃ preparation in [5] at temperatures near 900 K. Starting from a temperature of 950 K, YbBr₃⁻ 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 YbBr₃⁻ and YbBr₄⁻ ions becomes comparable, as was observed at the stage of the congruent vaporization of the initial preparation of YbBr₂ under study.

Even though there were molecules of ytterbium monobromide in the vapor, none of the stages of experiments with YbBr₃ and YbBr₂ revealed the presence of YbBr₂⁻ ions. These ions were not recorded in an additional experiment with the YbBr₂–Yb system.

The YbBr₂–LaBr₃ system for which the equilibrium constants of the gas-phase exchange ion–molecular reactions IV and V were obtained (Table 1) and in which LaBr₃ molecules and LaBr₄⁻ ions are considered standards [8, 20, 21], was studied to determine the enthalpies of formation of the negative YbBr₃⁻ and YbBr₄⁻ ions. The enthalpies of these reactions and the enthalpies of the formation of YbBr₃⁻ and YbBr₄⁻ ions as calculated according to the II law of thermodynamics are given in Tables 1 and 3. The thermodynamic functions of YbBr₄⁻ ions (Table 2) were estimated by a comparative method based on the functions LuBr₄⁻ [22]. The functions of YbBr₃⁻ ions were considered to correspond to the YbBr₃ 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 YbBr_2 and YbBr_3 molecules' affinity to the bromine anion were 2.7 ± 0.2 and 3.3 ± 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 $\text{Yb}-\text{Br}$ 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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