

SHORT
COMMUNICATIONS

Molecular and Ionic Sublimation of Erbium Tribromide

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Abstract—The molecular and ionic composition of vapor over erbium tribromide sublimed from the Knudsen effusion cell and the open surface of a single crystal was studied by high-temperature mass spectrometry. The partial pressures of ErBr_3 and Er_2Br_6 molecules in saturated vapor and the ratio between their sublimation coefficients under free vaporization conditions were determined. The enthalpies and activation energies of sublimation of ErBr_3 crystals in the form of monomers and dimers were calculated. The emission of ErBr_4^- and Er_2Br_7^- was recorded in studies of ionic sublimation in both modes. The enthalpies of formation of gas molecules and ions were determined.

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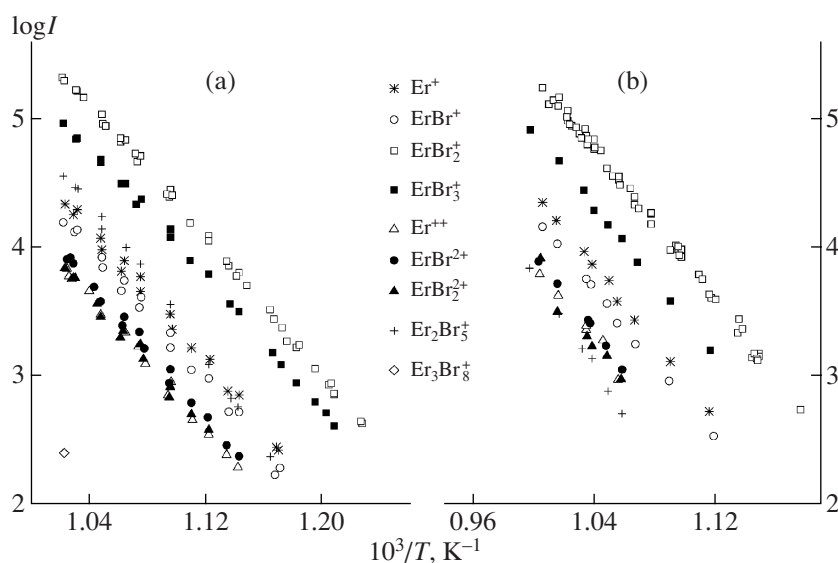
Systematic mass spectrometric studies of molecular and ionic sublimation of lanthanide tribromides were initiated in our recent works [1, 2] performed under the conditions of equilibrium (Knudsen's effusion method) and free vaporization from the open surface of LnBr_3 crystals (Langmuir method). Such a combined approach was used for the first time. The data obtained for lanthanum [1] and lutetium [2] tribromides demonstrated the possibility of increasing the reliability of thermodynamic data and allowed us to make assumptions about the mechanisms of molecular and ionic sublimation. The present paper is a continuation of these

studies and deals with changes in the thermodynamic and kinetic parameters in the series of LnBr_3 crystals.

This communication reports data on erbium tribromide. The synthetic and measurement procedures were described in detail in [1].

Molecular Sublimation

The figure shows the temperature dependences of electron impact mass spectra measured in the Knudsen and Langmuir modes. The major difference between these mass spectra lies in a considerably smaller fraction of complex ions (containing two and more erbium



Temperature dependences of ion currents in the electron impact mass spectra in the (a) Knudsen and (b) Langmuir modes.

Table 1. Thermodynamic functions $\Phi^\circ(T)$, J/(mol K), and $H^\circ(T) - H^\circ(0)$, kJ/mol

T, K	$\Phi^\circ(T)$	$H^\circ(T) - H^\circ(0)$	$\Phi^\circ(T)$	$H^\circ(T) - H^\circ(0)$	$\Phi^\circ(T)$	$H^\circ(T) - H^\circ(0)$	$\Phi^\circ(T)$	$H^\circ(T) - H^\circ(0)$
	ErBr ₃ (cr)		ErBr ₃ (g)		ErBr ₄ ⁻ (g)		Er ₂ Br ₇ ⁻ (g)	
298.15	125.00	26.00	338.51	20.40	369.87	26.42	545.69	51.01
800	216.79	79.00	410.01	61.62	463.74	80.09	723.86	155.52
900	228.51	90.24	419.38	69.89	475.58	90.86	746.74	176.48
1000	239.15	101.70	427.81	78.18	486.25	101.64	767.36	197.45
1100	248.91	113.38	435.40	86.47	495.97	112.42	786.08	218.44
1196	257.59	124.80	442.00	94.43	504.54	122.78	802.53	238.60

atoms) recorded under the conditions of sublimation from the open surface of a crystal compared with the fraction of complex ions recorded under equilibrium conditions. An analysis of the mass spectra by the standard procedure [1, 2] led us to conclude that the Er⁺, ErBr⁺, ErBr₂⁺, ErBr₃⁺, Er²⁺, ErBr₂²⁺, and ErBr₂²⁺ ions formed predominantly from ErBr₃ molecules. The Er₂Br₅⁺ and Er₂Br₄⁺ complex ions are the products of the ionization of Er₂Br₆ dimeric molecules; the Er₃Br₈⁺ ions are the products of the ionization of Er₃Br₉ trimeric molecules.

The partial pressures of molecules in vapor were calculated by the equation [1]

$$p_i = \frac{kT}{\sigma_i^{\text{mol}}} I_i, \quad (1)$$

where k is the instrument sensitivity constant (determined in a separate experiment with silver vaporization); T is the cell temperature; 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} [3]; $\sigma^{\text{mol}} = 0.75 \sum_j \sigma_j^{\text{at}}$ [4]); and I_i is the total current of ions of all types formed from the i th molecule.

The experimental data on saturated vapor pressures p (Pa) of monomeric and dimeric molecules were approximated by the equations

$$\begin{aligned} \log p(\text{ErBr}_3) &= (-13.456 \pm 0.078) \times 10^3/T \\ &+ (13.646 \pm 0.088), \end{aligned} \quad (2)$$

815–979 K;

$$\begin{aligned} \log p(\text{Er}_2\text{Br}_6) &= (-15.855 \pm 0.293) \times 10^3/T \\ &+ (14.938 \pm 0.318), \end{aligned} \quad (3)$$

859–979 K.

The number with the sign \pm is the standard deviation.

The enthalpies of sublimation of erbium tribromide in the form of monomeric and dimeric molecules were determined from the temperature dependences of the

partial pressures of the saturated vapor components using the procedure for processing the experimental data according to the second and third laws of thermodynamics.

The thermodynamic functions of condensed ErBr₃ were calculated by G. A. Bergman (United Institute of High Temperatures, Russian Academy of Sciences). The thermodynamic functions of gaseous ErBr₃ were calculated in the rigid rotator–harmonic oscillator approximation using molecular constants [5]. The functions for Er₂Br₆ dimeric molecules were evaluated by the comparative method using the procedure described in [2]. Table 1 lists the functions used in calculations.

Table 2 presents the results of processing the experimental saturated vapor pressures, including the literature data, for which we used the procedures of the second and third laws of thermodynamics based on a single set of thermodynamic functions. The original data of [6, 7] on the total vapor pressure were corrected for the partial pressures of monomeric molecules (the vapor composition was taken into account based on the $p(\text{ErBr}_3)/p(\text{Er}_2\text{Br}_6)$ ratio) using the data of the present study.

As can be seen from Table 2, the enthalpies of sublimation of monomeric molecules calculated using the second and third laws from the experimental vapor pressures obtained by different authors agree well with one another. A more detailed analysis was performed by determining the temperature behavior of the enthalpies of sublimation calculated by the third law and comparing the experimental (second law) and calculated (third law) entropies of sublimation [2]. This afforded the mean weighted value of $\Delta_s H^\circ(\text{ErBr}_3, 298.15) = 275 \pm 10$ kJ/mol, which was recommended for use. For dimeric molecules, agreement between the sublimation enthalpies is also satisfactory. For further calculations, it is recommended to use $\Delta_s H^\circ(\text{Er}_2\text{Br}_6, 298.15) = 341 \pm 30$ kJ/mol (the average over the values determined by the third law in this work and [11]).

Using the recommended enthalpies of sublimation of erbium tribromide and the literature value $\Delta_f H^\circ(\text{ErBr}_3, \text{cr}, 298.15 \text{ K}) = -837.1 \pm 3.0$ kJ/mol [8], we obtained $\Delta_f H^\circ(298.15 \text{ K})$ of gaseous monomeric and dimeric molecules, -562 ± 12 kJ/mol and $-1333 \pm$

Table 2. The enthalpies (kJ/mol) and entropies (J/(mol K)) of sublimation of ErBr₃ monomers and dimers and the enthalpies of ion-molecular reactions

ΔT , K	N	T_{mh}	2nd law			3rd law	Ref.
			$\Delta_s H^\circ(T_{av})$	$\Delta_s S^\circ(T_{av})$	$\Delta_s H^\circ(298.15)$	$\Delta_s H^\circ(298.15)$	
$ErBr_3(cr) = ErBr_3$							
815–979	39	893	257.5 ± 1.5	165.3 ± 1.7	272.1 ± 1.5	274.9 ± 12.0	This work
826–1035	98	919	278.1 ± 3.6	192.6 ± 3.4	293.4 ± 3.6	270.3 ± 12.0	[11]
919–1058	58	991	269.8 ± 2.9	170.1 ± 3.8	287.4 ± 2.9	282.7 ± 12.0	[6]
1242–1506		1361	186.7 ± 2.1	110.5 ± 2.7	271.7 ± 2.1	269.3 ± 12.0	[7]
938–1048		993	266 ± 4		282 ± 5	281 ± 2	[12]
$2ErBr_3(cr) = Er_2Br_6$							
859–979	14	922	304 ± 6	190 ± 6	324 ± 6	344 ± 40	This work
826–1035	98	919	339 ± 5	235 ± 5	359 ± 5	338 ± 40	[11]
938–1048		993	317 ± 13		337 ± 14	337 ± 20	[12]
$ErBr_3 + LaBr_4^- = ErBr_4^- + LaBr_3$							
959–1038	15	1006	-18.2 ± 23		-17.6 ± 23	-15.1 ± 5	This work
$Er_2Br_7^- = ErBr_4^- + ErBr_3(cr)$							
936–1085	25	1012	-72.8 ± 8		-82.2 ± 8	-77.5 ± 40	This work

Note: N is the number of measurements; T_{av} is the average harmonic temperature. For the values evaluated by the second law, the values with the sign \pm are the standard deviations; for the values evaluated by the third law, these are the limiting errors including the statistical error and the systematic error in the temperature, pressure, and the reduced Gibbs energy. The data of [12] are given in the original form.

30 kJ/mol, respectively. For ErBr₃ molecules, our value differs significantly from -505 ± 17 kJ/mol obtained [9] using the model of the valence state of *an atom in a molecule*.

The activation energies of sublimation of the erbium tribromide crystal in the monomeric and dimeric form were determined from the regression coefficients of the dependences $\log(\sum_j I_j T / a_j \gamma_j) - 1/T$; j : Er⁺, ErBr⁺, ErBr₂⁺, ErBr₃⁺, Er²⁺, ErBr²⁺, and ErBr₂²⁺, and $\log I_{Er_2Br_6^-} T - 1/T$, $E_s(ErBr_3, 931 \text{ K}) = 290 \pm 2$ kJ/mol and $E_s(Er_2Br_6, 970 \text{ K}) = 360 \pm 10$ kJ/mol, respectively. The enthalpies of sublimation were slightly higher than the corresponding values for erbium tribromide determined in this work. This difference is similar to the situation observed in our previous work, where we compared the energy characteristics of sublimation of the lutetium tribromide crystal [2]; this is probably explained by changes in the structure of the kinks (fractures of vaporization steps) on the crystal surface in different sublimation modes, or this may be a consequence of the temperature dependence of the sublimation coefficients.

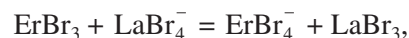
The relative change in the sublimation coefficients was analyzed by comparing the ratio $j(Er_2Br_6^-)/j(ErBr_3)$ of the molecular fluxes from the surface of ErBr₃ in the Knudsen and Langmuir modes; it was shown that, at 1000 K, the ratio was 1.17×10^{-1} and 1.67×10^{-2} ,

respectively. This decrease in the fraction of sublimed dimeric molecules on passing from dynamic equilibrium conditions to sublimation from an open surface allowed us to evaluate the ratio between the sublimation coefficients of dimers and monomers, $\alpha_s(Er_2Br_6^-)/\alpha_s(ErBr_3) = 7$.

Ionic Sublimation

As in previous studies of lanthanum and lutetium tribromides [1, 2], we observed thermal emission of ErBr₄⁻ and Er₂Br₇⁻ in both modes. Moreover, in the Knudsen mode, the mass spectrum contained signals of more complex oligomeric ions Er₃Br₁₀⁻ and Er₄Br₁₃⁻ and also signals of Br⁻ ions of nonequilibrium origin [1, 2].

To obtain the enthalpies of formation of ErBr₄⁻ and Er₂Br₇⁻ by the procedure described previously [10], we determined the enthalpies (Table 2) of the ion molecular reactions



(The first reaction was studied in an additional experiment with the LaBr₃–ErBr₃ system.) Based on the enthalpies of the reactions (third law), we found that

$\Delta_f H^\circ(\text{ErBr}_4^-, \text{g}, 298.15 \text{ K}) = -1098 \pm 22 \text{ kJ/mol}$ and $\Delta_f H^\circ(\text{Er}_2\text{Br}_7^-, \text{g}, 298.15 \text{ K}) = -1876 \pm 47 \text{ kJ/mol}$. To calculate the thermodynamic functions of LaBr_4^- , ErBr_4^- , and Er_2Br_7^- ions (Table 1), we used the approaches similar to those described previously [1, 2]. For calculations, we used the following enthalpies of formation $\Delta_f H^\circ(298.15 \text{ K})$, kJ/mol: -584 ± 10 (LaBr_3) [1, 8] and -1105 ± 14 (LaBr_4^-) [1].

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