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CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

Thermodynamic Parameters of Vaporization of $EuBr_2$

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Abstract—The vaporization process of europium dibromide was studied using high-temperature mass spectrometry. It was ascertained that saturated vapor in temperature range of 1049–1261 K was represented mainly by $EuBr_2$ molecules; the fraction of dimer molecules Eu_2Br_4 was less than 1%. Heat capacities of solid and liquid europium dibromide, as well as the melting enthalpy were measured by means of differential scanning calorimetry in temperature range 300–1100 K; using these data thermodynamic functions for $EuBr_2$ in condensed state were calculated. For all experimental data, including the literature data, thermodynamic characteristics of the vaporization of europium dibromide were determined using a unified set of thermodynamic functions according to the methods of the second and third laws of thermodynamics. The value of $\Delta_s H°(298.15\ K) = 354 \pm 5$ kJ/mol was recommended for the reaction of sublimation of $EuBr_2(cr.) = EuBr_2$.

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INTRODUCTION

Unlike lanthanide tribromides [1–3], there are no published reliable thermodynamic characteristics of the vaporization of Eu, Yb, and Sm dibromides, which are known to exist stably in the bivalent state [4]. This is due on the one hand to a lack of experimental data on the pressure and composition of saturated vapor over $LnBr_2$, and on the other hand to the estimated character of thermodynamic functions of these compounds both in gas and condensed phases. Data on the pressure of saturated vapor has been obtained only for $EuBr_2$ in measurements for the collection and analysis procedures of effusate from a Knudsen chamber [5, 6] and effusion measurements with mass spectrometry recording of vaporization products [7]. Absolutely no studies on the regularities of the vaporization of $YbBr_2$ and $SmBr_2$ have so far been performed. There are only estimated values for the temperature dependence of heat capacity for all $LnBr_2$ compounds.

We therefore began systematic thermodynamic investigations of the evaporation of europium, ytterbium, and samarium dibromides using high-temperature mass spectroscopy and differential scanning calorimetry. In this study, new experimental data for $EuBr_2$ were obtained, and a critical analysis of the calculated thermodynamic characteristics of vaporization was carried out on the basis of all available literature data, using a unified set of updated thermodynamic functions.

EXPERIMENTAL

The vaporization of $EuBr_2$ was studied on an MI-1201 serial magnetic mass spectrometer (∠90°, curvature radius of 200 mm) equipped with an evaporator and a Knudsen effusion chamber. The instrument was described in more detail in [8]. Mass spectra were recorded at energy of ionized electrons E_e, varied over the range of $E_e = 0–70$ eV, and an emission current from the cathode of 1 mA. The system for the registration of ion currents consisted of a secondary electron multiplier combined with a Keithley picoampermeter. The sensitivity of the registration scheme was 10^{-17} A. The temperature of the effusion cell was measured using a standard tungsten–rhenium thermocouple calibrated in melting points of pure NaBr and Ag. The sample was loaded into an inert graphite cell preannealed under vacuum. The cross section area of the cell related to the area of the infusion hole (0.16 mm^2) was estimated by a factor of ~300. Instrument calibration was performed according to the internal standard procedure using metallic silver as the reference.

The values of temperature, melting heat, and heat capacity of $EuBr_2$ in the condensed state were measured on a Calvet-type DSC 121 Setaram differential

Table 1. Mass spectra and ion appearance energies

T, K	E_e, eV	I, %				References
		Eu^+	$EuBr^+$	$EuBr_2^+$	$Eu_2Br_3^+$	
1212	70	20	100	16	0.32	Our data
1212	35	42	100	18	0.015	[7]
–	–	50	100	15		[5]
AE, eV		14.3	10.1	9.3		Our data
			10.4			[5]

Note: Mass spectra are given with consideration for the isotopic modification of ions. Inaccuracy in AE is assessed to be ±0.5 eV; I is relative intensity of ion current, %.

scanning calorimeter (DSC). The instrument was described in more detail in [9, 10]. The calibration of the experimental temperature scale was carried out using metals with purity grades of no less than 99.999% (In, Sn, Pb, Zn, Sb, Al), the melting temperatures of which covered the range of working temperatures of the instrument. Moreover, the same references were used to determine temperature corrections that took into account the effect of heating/cooling rate on temperatures measured. The measurements were made at different rates of temperature change.

Temperature and enthalpy calibrations of the DSC 121 were carried out using references with deviations correspondingly no higher than ±1 K and ±1%. To measure heat capacity C_p°, we used the stage heating method [11, 12], according to which small temperature rises were interlaced with its isothermic delays, intended for the attainment of heat equilibrium by the sample under study. For $EuBr_2$, each temperature stage amounted to 5 K with a delay duration of 400 s. The measurements were performed over the temperature range 300–1100 K. The difference in the masses of the quartz cells (400–500 mg) was less than 1 mg. Melting temperature and enthalpy were measured at heating and cooling rates of 1–5 K/min. All manipulations with $EuBr_2$, being extremely hydroscopic, were performed in a dry glove box under argon atmosphere.

The $EuBr_2$ samples under investigation were synthesized using the familiar NH_4Br procedure [13, 14], which included the following stages: dissolution of Eu_2O_3 (Fluka, 99.9%) in HBr; introduction of ammonium bromide in Eu : NH_4Br ratio of 1 : 3.5, followed by vaporization of the solution; grinding of the residue ($(NH_4)_3EuBr_6$) and its heating to 180°C in argon flow and to 400°C under vacuum, yielding the mixture of $EuBr_2$ and $EuBr_3$; and additional annealing under vacuum at 500°C until $EuBr_3$ completely disintegrated into $EuBr_2$ and Br_2 was released. The product obtained was verified using X-ray and chemical tests (mercurimetric analysis for bromine and complexonometric analysis for europium) with the following results: Eu, 48.74 ± 0.13% (theoretical value of 48.75%); Br, 51.26 ± 0.12% (theoretical value of 51.25%).

RESULTS AND DISCUSSION

The relative intensities of ion currents of Eu^+, $EuBr^+$, $EuBr_2^+$, and $Eu_2Br_3^+$ registered in electron-impact mass spectra of the molecules are listed in Table 1, together with the data from [5, 7].

The ion appearance energies (AE) obtained by linear extrapolation of threshold regions of curves of ionization efficiency (Fig. 1) using silver as the reference to calibrate the energy scale of ionizing electrons are also given (Table 1). The temperature dependences of ion currents measured over the range 1049–1261 K are shown in Fig. 2.

An analysis of the coefficients of the linear equation employed to approximate ion currents,

$$\ln I = -A \times 10^3/T + B \quad (1)$$

(Table 2), the AE values, and the shapes of the curves of ionization efficiency (which contain no pronounced kinks), leads us to conclude that Eu^+, $EuBr^+$, and $EuBr_2^+$ ions are formed from $EuBr_2$ molecules, while $Eu_2Br_3^+$ ions are products of the dissociative ionization of Eu_2Br_4 molecules. The difference in the relative ion currents of Eu^+, $EuBr^+$, and $EuBr_2^+$ obtained by different authors might be the result of using different ionization energies, or of differences in the geometry of ion sources, the mutual dimensional orientation of molecular, electron, and ion beams, and pecu-

Table 2. Coefficients of Eq. (1). N is the number of measurements

Ion	A	B	N	T, K
Eu^+	15.67 ± 0.44	14.99 ± 0.38	13	1079–1261
$EuBr^+$	15.20 ± 0.25	15.34 ± 0.22	18	1049–1261
$EuBr_2^+$	14.16 ± 0.32	13.76 ± 0.27	13	1110–1259

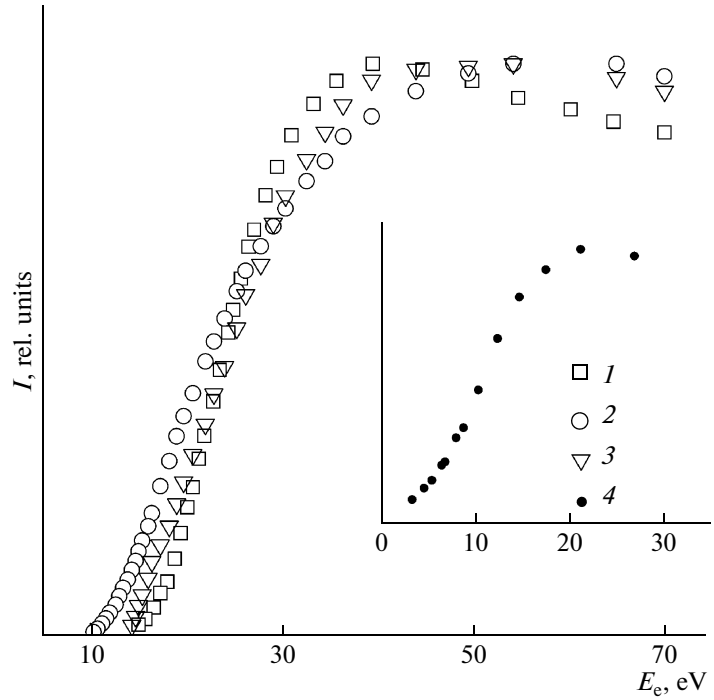

Fig. 1. Curves of ionization efficiency for $EuBr_2$: (*1*) Eu^+; (*2*) $EuBr^+$; (*3*) $EuBr_2^+$; (*4*) Ag^+ (reference).

liarities in the focusing of the ion optical system. The appreciably lower fraction of $Eu_2Br_3^+$ in the mass spectrum given in [7] is of interest. (This distinction is discussed below.)

The partial pressures of molecules in vapor were calculated using the standard mass spectrometric procedure with the electron-impact ionization of molecules on the basis of relation

$$p_i = \frac{kT}{\sigma_i^{\text{mol}}} \sum_j \frac{I_{ij}}{\gamma_j a_j}, \quad (2)$$

where k is the sensitivity constant of the instrument, T is the cell temperature, σ^{mol} is total ionization cross section of the ith molecule with the working energy of ionizing electrons (calculated on the basis of ionization cross sections of atoms σ^{mol} [15] using the expression [16] $\sigma^{\text{mol}} = 0.75\sum_j \sigma_j^{\text{at}}$); $\sum_j I_{ij}/(a_j\gamma_j)$ is the total ion current of ions of all types formed from molecule i, a is the coefficient taking into account the natural abundance of isotopes of the measured ion, and γ is the coefficient of ion–electron conversion (it is assumed that $\gamma \sim qM^{-1/2}$ [17], where q and M are, respectively, the charge and molecular mass of ion).

The calculated partial pressures p (Pa) of $EuBr_2$ molecules in saturated vapor over liquid europium dibromide over the range of 1049–1261 K are approximated by equation

$$\ln p(EuBr_2) = (-36.224 \pm 0.643) \times 10^3/T + (18.611 \pm 0.558). \quad (3)$$

The standard deviation is denoted by sign ±.

The pressure of dimer molecules is less than 1% of the total pressure and amounts to 2.4×10^{-3} Pa at $T = 1212$ K.

Figure 3 shows the generalization of all available results on temperature dependences $p(EuBr_2)$, including data from mass-spectrometric investigations [7] and the data of [5, 6] on the overall pressure of vapor, which can relate to the pressure of $EuBr_2$ molecules due to the small ratio of dimer molecules in vapor. We can see in Fig. 3 that the value of $p(EuBr_2)$ in this study seems to be considerably higher than that in [5–7]. (An analysis of the reasons for such disagreement is given below.)

In order to determine the enthalpies and entropies of vaporization of europium dibromide using procedures of processing experimental data by the second and third laws of thermodynamics, we calculated the thermodynamic functions for gaseous and condensed $EuBr_2$. Functions $\Phi'(T) = -(G^\circ(T) - H^\circ(298.15\text{ K}))/T$ and $H^\circ(T) - H^\circ(298.15\text{ K})$ of gaseous molecules (Table 3) were calculated in the rigid rotator–harmonic oscillator (RRHO) approximation using molecular parameters obtained by gas electronography [18]: type of symmetry for equilibrium configura-

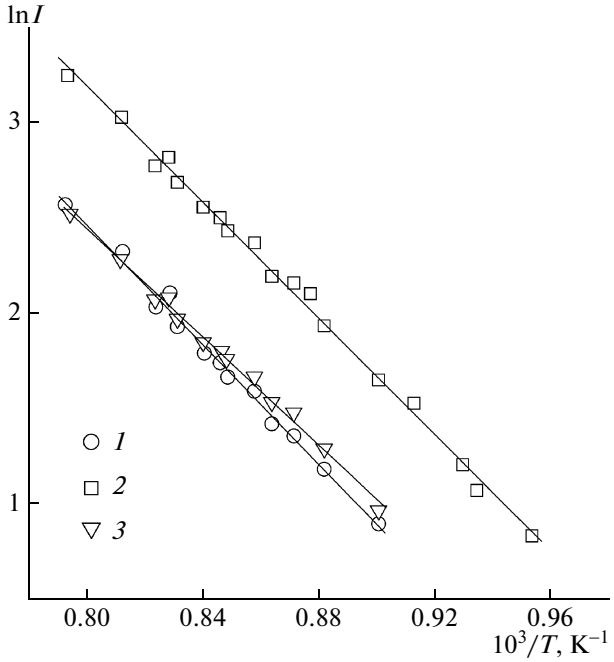

Fig. 2. Temperature dependences of ion currents: (*1*) Eu^+; (*2*) $EuBr^+$; (*3*) $EuBr_2^+$.

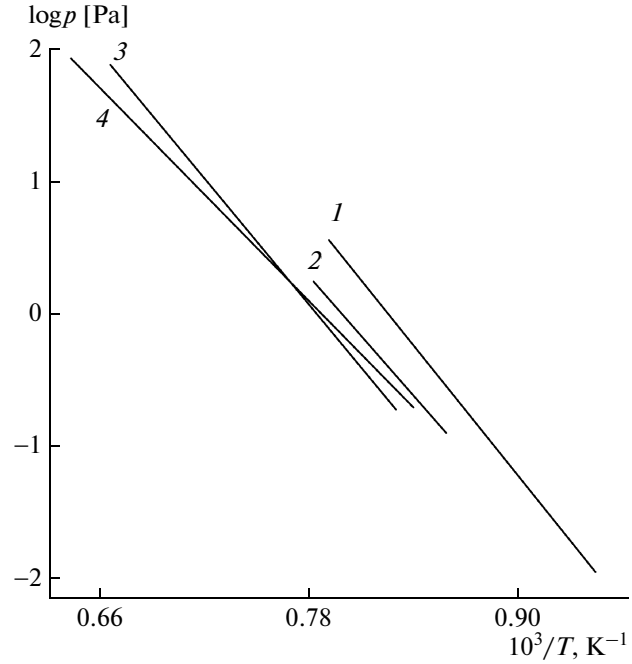

Fig. 3. Temperature dependences of saturated vapor pressure over $EuBr_2$: (*1*) our data; (*2*) [7]; (*3*) [6]; (*4*) [5].

tion C_{2v}, r(Eu–Br) = 2.767 ± 0.006 Å, ∠Br–Eu–Br = 135.0 ± 3.5°, ν_1 = 225 ± 10 cm^{-1}, ν_2 = 40 ± 4 cm^{-1}, ν_1 = 223 ± 10 cm^{-1}; the electronic state was assumed to be high-spin (a statistical weight of 8). The errors in functions of Gibbs reduced energy were calculated on the basis of two components [16]: (1) the error stipulated by approximate characters of calculation in RRHO method accepted to be 5%; (2) the error stipu-

Table 3. Thermodynamic functions $C_p^\circ(T)$, $S^\circ(T)$, $\Phi'(T)$ (J mol^{-1} K^{-1}) and $H^\circ(T) - H^\circ(298.15\ K)$ (kJ mol^{-1}) for $EuBr_2$ in condensed and gaseous states

$EuBr_2$ (cond.)					$EuBr_2$ (gas)				
T, K	$C_p^\circ(T)$	$S^\circ(T)$	$\Phi'(T)$	$H^\circ(T) - H^\circ(298.15)$	T, K	$C_p^\circ(T)$	$S^\circ(T)$	$\Phi'(T)$	$H^\circ(T) - H^\circ(298.15)$
298.15	76.27	136.91	136.91	0	298.15	56.65	355.24	355.24	0
400	77.12	159.45	139.92	7.81	400	57.32	371.99	357.47	5.81
500	77.95	176.74	145.61	15.56	500	57.63	384.82	361.70	11.55
600	78.78	191.03	152.03	23.40	600	57.80	395.34	366.46	17.33
700	79.61	203.23	158.49	31.32	700	57.91	404.26	371.24	23.11
800	80.44	213.92	164.77	39.32	800	57.97	412.00	375.86	28.91
900	81.27	223.44	170.77	47.41	900	58.02	418.83	380.26	34.71
941	81.61	227.07	173.14	50.75					
941	105.39	250.69	173.14	72.97					
1000	105.39	257.10	177.91	79.19	1000	58.06	424.95	384.433	40.51
1100	105.39	267.14	185.57	89.72	1100	58.08	430.48	388.372	46.32
1200	105.39	276.31	192.75	100.26	1200	58.10	435.54	392.095	52.13
1300	105.39	284.75	199.51	110.8	1300	58.12	440.19	395.618	57.94

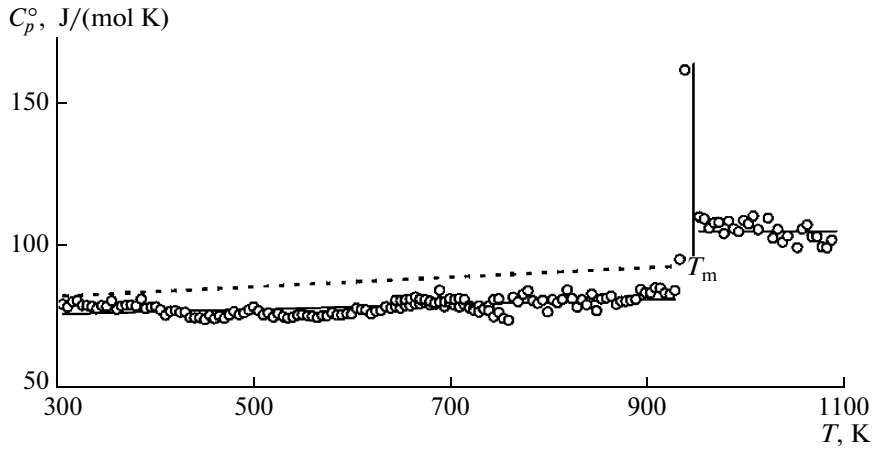

Fig. 4. Molar heat capacity of $EuBr_2$. Dots represent the experimental data; the solid line represents the approximation equation; the dotted line corresponds to the data in [6].

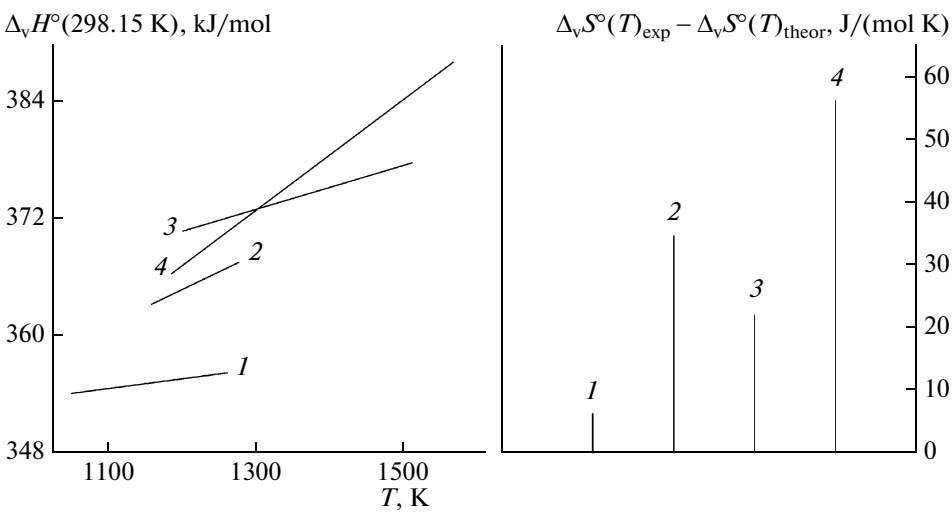

Fig. 5. Results from the analysis of the temperature course for values $\Delta_v H^\circ(EuBr_2, 298.15)$ and difference $\Delta_s S^\circ(EuBr_2, T)_{exp} - \Delta_s S^\circ(EuBr_2, T)_{theor}$: (*1*) our data; (*2*) [7]; (*3*) [6], (*4*) [5].

lated by discrepancies in moments of inertia and oscillation frequencies, calculated using equation

$$\frac{\delta\Phi'(T)}{R}\left\{\left[\frac{\delta(I_A I_B I_C)}{2 I_A I_B I_C}\right]^2 + \sum_{i=1}^{n}\left[d_i \frac{[H^\circ(T) - H^\circ(298.15)]_{\text{h.o.},i}}{RT}\frac{\delta\nu_i}{\nu_i}\right]^2\right\}^{1/2}, \quad (4)$$

where d_i is the degeneracy of the ith oscillation, ν_i is its fundamental frequency, $H^\circ(T)-H^\circ(298.15)$ is the enthalpy of the ith harmonic oscillator, and $\delta(I_A I_B I_C)$ is the inaccuracy in the product of moments of inertia (taken to be 10%). The inaccuracy in value Φ'(1000 K) estimated using this procedure amounted to 4.5 J mol^{-1} K^{-1}.

To perform calculations of functions of $EuBr_2$ in condensed phase we used the results of DSC measurements [19]. In these measurements, only the endothermic peak corresponding to the melting of $EuBr_2$ was registered on the thermograms. The values of the melting temperature and enthalpy were, respectively, 941 K and 22.2 ± 0.4 kJ mol^{-1}. Experimental data on the temperature dependence of the heat capacity of $EuBr_2$ are shown in Fig. 4. They can be linearly approximated over the temperature range up to the melting point with an accuracy of ±2.25 J mol^{-1} K^{-1} (standard deviation) by the equation

$$C_p^\circ = 73.79 + 8.31 \times 10^{-3} T. \quad (5)$$

For the liquid phase of $EuBr_2$, the heat capacity was averaged and assessed by the constant value C_p° =

Table 4. Enthalpies (in kJ mol^{-1}) and entropies (in J mol^{-1} K^{-1}) of vaporization/sublimation reaction $EuBr_2$(l/cr) = $EuBr_2$

T, K	T_{ah}	Second law			Third law	References
		$\Delta_v H°(T_{ah})$	$\Delta_v S°(T_{ah})$	$\Delta_s H°$(298.15 K)	$\Delta_s H°$(298.15 K)	
1049–1261	1153	301.2 ± 5.3	154.7 ± 4.6	347.2 ± 5.8	354.4 ± 5.0	Our data
1158–1276	1230	272.5 ± 2.6	123.4 ± 2.2	331.4 ± 3.4	365.9 ± 5.0	[7]
1220–1512	1366	288.7 ± 2.9	130.9 ± 2.1	344.7 ± 3.7	374.9 ± 5.0	[6]
1185–1568	1377	243.8 ± 3.2	96.4 ± 2.3	300.3 ± 3.9	377.7 ± 4.5	[5]

Note: Sign ± refers to the following errors: in calculations using the second law for $\Delta_v H°(T_{ah})$, the standard deviation; for $\Delta_s H°$(298.15 K), the error $\Delta_v H°(T_{ah})$ was supplemented with the error of the increment of enthalpy of vaporization reaction; in calculations using the third law, the error determined by the estimated inaccuracy of reduced Gibbs energy of vaporization reaction; T_{ah} is the average harmonic temperature.

105.39 ± 3.32 J mol^{-1} K^{-1}. It is notable that the only estimated value of the heat capacity of crystalline $EuBr_2$ that has been published [6] is systematically inflated, compared to our data over the entire temperature range (Fig. 4).

Thermodynamic functions of $EuBr_2$ in condensed state calculated over the temperature range of 298–1300 K are listed in Table 3. The value of $S°$($EuBr_2$, cr, 298.15 K) = 136.91 J mol^{-1} K^{-1} was taken from [6].

The thermodynamic characteristics of vaporization/sublimation of $EuBr_2$ were determined using the procedure of processing experimental data by the second and third laws on the basis of the original data on pressure p($EuBr_2$) of this investigation and studies [5–7]. using a unified set of our own thermodynamic functions. These characteristics are listed in Table 4. As can be seen, the agreement between the values of $\Delta_s H°$(298.15 K) determined using the two procedures was observed only in this study. The enthalpies determined using the third law on the basis of data [5–7] find no agreement in the range of assessed inaccuracies. The reason for this disagreement is associated with the difference in absolute pressures p($EuBr_2$) mentioned earlier.

The pressure of vapor over the individual compounds being measured is known to depend to an appreciable extent on the purity of the investigated samples. The occurrence of impurities may result in its considerable reduction. We may also expect a reduction in the dimer fraction in vapor in relation to the fraction of monomer molecules. This is the situation that is observed when compared with [5, 7]. Note that in work [5], where the lowest pressure p($EuBr_2$) was obtained, no dimer molecules were registered in the vapor. Our more detailed analysis of the results is based on the detection of the temperature course of sublimation enthalpies calculated according to the third law, and on our comparison of sublimation entropies experimentally determined using the second law with those theoretically calculated [20]. The results of this analysis are shown in Fig. 5. As can be seen, such an approach attests to the high reliability of the results of this investigation, notably, the minimum temperature course for the value $\Delta_s H°$(298.15 K) and the minimum difference between the experimental and theoretically calculated entropy of sublimation are observed. For the reaction of sublimation $EuBr_2$(cr.) = $EuBr_2$ the value $\Delta_s H°$(298.15 K) = 354 ± 5 kJ/mol is thus recommended.

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