Thermodynamic, thermochemical and thermophysical properties of HgBr$_2$

Anton Kozma[1*],

Antonina Malinina[2],

Evgeniy Golub[3],

Vasylyna Rusyn[4],

Nelya Golub[1],

Vitalii Dziamko[1],

Viktoriia Dziamko[5],

Oleksandr Malinin[2],

Andrii Solomon[6]

[1] *Department of Physical and Colloid Chemistry,*
Uzhhorod National University,
46 Pidhirna Street,
88000 Uzhhorod, Ukraine

[2] *Department of Quantum Electronics,*
Uzhhorod National University,
54 Voloshyna Street,
88000 Uzhhorod, Ukraine

[3] *Department of Pharmaceutical Disciplines,*
Uzhhorod National University,
46 Pidhirna Street,
88000 Uzhhorod, Ukraine

[4] *Department of Analytical Chemistry,*
Uzhhorod National University,
46 Pidhirna Street, 88000 Uzhhorod, Ukraine

[5] *Department of Mathematics and Informatics,*
Ferenc Rakoczi II Transcarpathian
Hungarian Institute,
6 Kosuta Square, 90200 Berehovo, Ukraine

[6] *Institute of Electron Physics,*
National Academy of Sciences of Ukraine,
21 Universytetska Street, 88017 Uzhhorod, Ukraine

For mercury dibromide HgBr$_2$, a promising component of the working mixture of gas-discharge exciplex sources of coherent (lasers) and spontaneous (exciplex lamps) radiation, as well as a promising nonlinear optical crystal for the infrared radiation process, thermodynamic and thermochemical properties in the temperature range 173–512 K were investigated. The established basic thermodynamic (isobaric heat capacity C_p, total entropy S, enthalpy H and Gibbs energy G) and thermochemical (enthalpy ΔHf and Gibbs energy ΔGf of formation) functions of HgBr$_2$ were compared with the known literature data at 298–514 K. The obtained results differed from the literature within 1–2% (for C_p), 0.1–0.2% (for S, H and G) and 0.1–0.6% (for ΔHf and ΔGf). The experimental data, combined with semi-empirical approaches and *ab initio* calculations taken from the literature, were used to estimate the previously unknown additional thermodynamic and thermophysical properties of HgBr$_2$: isochoric heat capacity C_V, Debye temperature θ_D, volume thermal expansion α_V, isothermal compressibility β_T (isothermal bulk modulus $B^T = 1/\beta_T$), Grüneisen constant γ_G, phonon longitudinal v_p, transverse v_s, average $\bar{v}$ velocities and phonon thermal conductivity κ. In the present work, it was found that crystalline mercury dibromide expands strongly upon heating and has a low phonon thermal conductivity.

Keywords: mercury dibromide, isobaric heat capacity, thermodynamic and thermochemical functions, thermophysical properties

* Corresponding author. Email: anton_kozma@yahoo.com;
anton.kozma@uzhnu.edu.ua

INTRODUCTION

Mercury dibromide $HgBr_2$ can be an effective component of promising exciplex sources of coherent (lasers) and spontaneous (excilamps) with record radiation power in the visible and infrared spectral regions [1–5]. In addition, mercury dibromide has an important environmental function, which is to remove free mercury from man-made objects. In particular, it is in the form of $HgBr_2$ that Hg is adsorbed from flue gases of coal-fired power plants [6, 7]. Hence, the hypothetical possibility of absorbing mercury from the environment in the form of $HgBr_2$ for its subsequent use in laser devices. This makes mercury dibromide an interesting material for a comprehensive physicochemical study.

It should be noted that $HgBr_2$ has been studied insufficiently. For example, in the scientific literature, there are only approximate thermodynamic data for $HgBr_2$ [8, 9], which are based mainly on the results of Refs. [10, 11]. However, works [10, 11] have some drawbacks. Thus, in Ref. [10], up to a temperature of 507 K, the change in enthalpy was studied only in two narrow intervals 298–304 K and 487–507 K. Probably, in Ref. [9], the valid isobaric heat capacity of mercury dibromide was calculated by differentiating the enthalpy values from Ref. [10] (note: Ref. [9] does not detail the process of obtaining the $C_p(HgBr_2)$ values from Ref. [10]). In turn, work [11] gives a single value, most likely not the valid, but only the average heat capacity of $HgBr_2$ for a long range 273–479 K. That is, in sources [10, 11] there are only a few experimental points, on the basis of which the values of $C_p(HgBr_2)$ were fitted in references [8, 9] for a wide temperature range 298–514 K. In addition, the analytical part of publication [10] shows that the thermal properties of mercury dibromide can differ significantly (by more than 20%) depending on the method used. This is important to consider when comparing different results.

As we can see, previously published works did not use direct studies of the valid heat capacity of $HgBr_2$. It should also be noted that the thermophysical parameters of mercury dibromide (thermal expansion and compressibility, thermal conductivity, etc.) remain unexplored, despite the significant prospects for the practical use of this compound.

The aim of this work was to directly measure the valid isobaric heat capacity and determine the related thermodynamic, thermochemical and thermophysical properties of $HgBr_2$.

EXPERIMENTAL

Mercury dibromide was obtained according to the method used at Uzhhorod National University [12]. $HgBr_2$ was identified by the classical methods of differential thermal analysis (DTA) and X-ray diffraction (XRD) analysis. The melting point determined by the DTA method [13] was compared with the data of other scientists [8–11, 14, 15]. According to the XRD method [13], using a conventional Bragg–Brentano powder diffractometer (Ni-filtered CuKα radiation with λ = 0.1541 nm) the experimental diffractogram was indexed. For this purpose, the known crystal structure data were taken from Refs. [16, 17]. The powder pattern analysis was performed using the personal computer programs POWDERCELL 2.0 [18] and UNITCELL [19]. The isobaric heat capacity was measured using an IT-S-400 device in the temperature range 173–498 K. Based on the experimental heat capacity, the basic thermodynamic and thermochemical functions of the studied compound were calculated. Using the established experimental physicochemical amounts, as well as the results of the known *ab initio* ELATE calculations by Gaillac et al. [20, 21] and semi-empirical methods [22–25], we evaluated additional thermodynamic (isochoric heat capacity, Debye temperature, Grüneisen constant) and thermophysical (volume thermal expansion, isothermal compressibility, phonon velocities and phonon thermal conductivity) properties of $HgBr_2$.

RESULTS AND DISCUSSION

Physicochemical analysis of $HgBr_2$

The DTA results for mercury dibromide are shown in Fig. 1.

When the test sample was monotonously heated from 293 to 563 K, the only effect (endothermic) was observed at 512 K (Fig. 1). The recorded temperature can be attributed to the melting point of $HgBr_2$. This result is in good agreement with the literature [8–11, 14, 15], according to which mercury dibromide melts congruently at
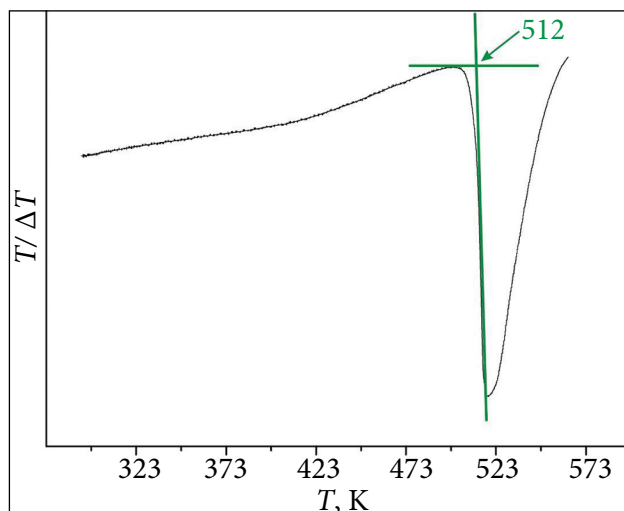
**Fig. 1.** Thermogram of the heating process of $HgBr_2$

514 K [8, 9], 511 K [10], 508 K [11], or 509 K [14, 15]. Our result differed from Refs. [8–11, 14, 15] within 1–4 K or 0.20–0.78%.

The results of the XRD study of $HgBr_2$ are presented in Fig. 2 and Table.

As can be seen from Fig. 2, the main reflexes of the experimental diffractogram of mercury dibromide are in good agreement with the data of other scientists [16, 17]. For a more detailed comparison, the basic reflexes of $HgBr_2$ were indexed (Table).

According to the data in the Table and using the UNITCELL program [19], the unit cell parameters of the analyzed $HgBr_2$ (orthorhombic crystal system, all angles equal to 90° [16, 17]) were calculated: $a = 0.4629$ nm, $b = 0.6806$ nm, $c = 1.2466$ nm and $V = 0.3928$ nm³. Let us compare them with the data of Braekken [16] and Werweel and Bijvoet [17]: $a = 0.4624$ nm, $b = 0.6789$ nm, $c = 1.2445$ nm, $V = 0.3907$ nm³ [16] and $a = 0.4670$ nm, $b = 0.6850$ nm, $c = 1.2450$ nm, $V = 0.3983$ nm³ [17]. As we can see, most of our results are intermediate compared to those of Refs. [16, 17], but closer to the data of Braekken [16]. Thus, the minimum difference between this work and [16] is 0.11%, and the maximum is 0.54%. The minimum difference between our results and [17] is close to 0.13%, and the maximum difference is 1.38%. It should be noted that the differences between the data [16] and [17] are in the wider range 0.04–1.91%.

Thus, the results of the physicochemical analysis confirmed the individuality of mercury dibro-
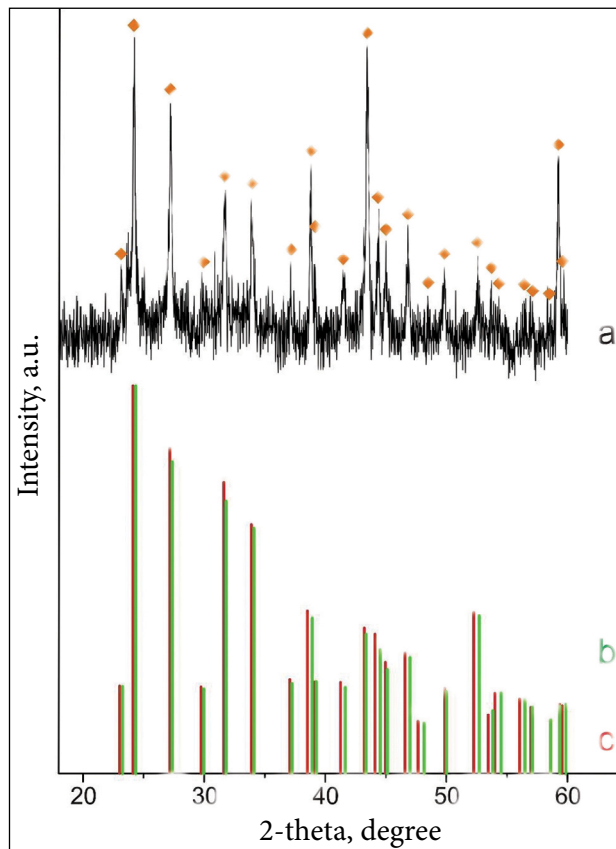
Fig. 2. X-ray diffraction data of $HgBr_2$: a (black lines) is an experimental diffractogram (this work), orange diamonds indicate the main analytical reflexes; b (green lines) is a bar chart by data of Braekken [16]; c (red lines) is a bar chart by data of Werweel and Bijvoet [17]

mide, which was used for further thermodynamic, thermochemical and thermophysical studies.
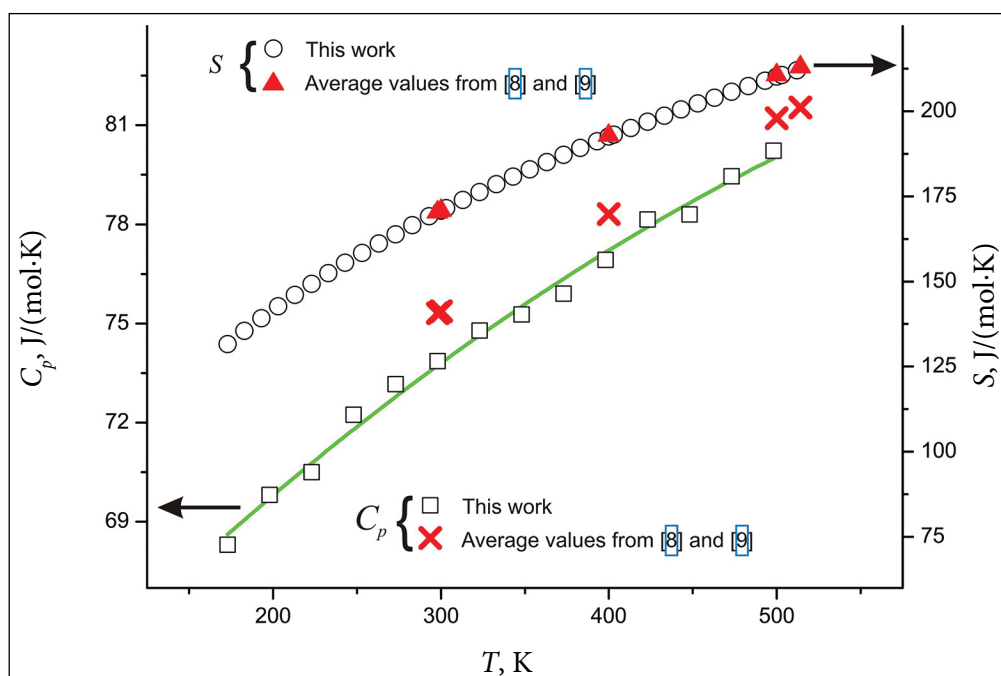
Basic thermodynamic and thermochemical properties of $HgBr_2$

The experimental values of the measured valid isobaric heat capacity of $HgBr_2$ are shown in Fig. 3, white squares. Note that in this work we used a simplified notation for the basic thermodynamic functions: C_p, S, H, etc. Similar notations were used in one of the classical thermochemical reference books [8]. In addition, all of the properties given here refer to the standard atmospheric pressure 0.1 MPa [8, 9].

Our results were compared with the average values from Refs. [8, 9] (Fig. 3, red crosses). It should be noted that Refs. [8, 9] contain almost identical (with differences within 0.0–0.2%) values of $C_p(HgBr_2)$. This is due to the use of the same initial data from Refs. [10, 11] in Refs. [8, 9]. It should also be noted that in this work all comparisons were made only for crystalline mercury

Table. **Indexing of the HgBr₂ X-ray diffractogram**

Basic h k l (by data [16–18])	2-theta, degree This work	2-theta, degree By Braekken [16]	2-theta, degree By Werweel and Bijvoet [17]
1 1 0	23.15	23.26	23.03
1 1 1	24.21	24.34	24.13
1 1 2	27.23	27.36	27.17
0 2 2	29.94	29.96	29.75
1 1 3	31.69	31.81	31.64
0 2 3	33.97	34.10	33.91
1 1 4	37.17	37.24	37.08
2 0 0	38.84	38.92	38.53
0 2 4	39.17	39.25	39.07
2 0 2	41.47	41.64	41.26
1 1 5	43.45	43.35	43.21
1 3 0	44.36	44.54	44.11
0 2 5	45.03	45.13	44.97
1 3 2	46.83	46.99	46.58
2 2 1	48.48	48.14	47.66
1 1 6	49.82	49.99	49.86
2 2 3	52.55	52.70	52.25
1 3 4	53.73	53.83	53.45
0 4 1	54.35	54.52	54.01
2 2 4	56.42	56.47	56.04
1 1 7	57.12	57.09	56.97
1 3 5	58.48	58.59	–
0 0 8	59.23	59.36	59.34
2 0 6	59.60	59.86	59.55

Fig. 3. Dependences of the isobaric heat capacity and the standard entropy on temperature for HgBr₂

dibromide. In Refs. [8, 9], the thermodynamic and thermochemical functions of gaseous [8, 9] and liquid [9] $HgBr_2$ at temperatures from 298 K (from 100 K for gas [9]) to over 600 K are additionally considered.

At the base temperatures 298, 300, 400 and 500 K, which were chosen in Refs. [8, 9], our values of $C_p(HgBr_2)$ differed from those in the literature within 1–2%. The maximum difference 1.9% was observed at 298 K. With increasing temperature, the difference decreased and was minimal (~1.2%) at the melting point of mercury dibromide. According to the well-known publications [26, 27], differences between the values of the heat capacity of up to 3–4% are acceptable. Thus, the results of this work confirmed the applicability of the fitting method used in Refs. [8, 9] for $HgBr_2$. However, our studies made it possible to describe the properties of mercury dibromide at low temperatures 173–298 K, which are not available in Refs. [8, 9].

The experimental data (white squares in Fig. 3) were described by various interpolation equations: the classical Maier–Kelley expression [28] and polynomials of degrees 1–3. It turned out that the highest determination index R^2 [29] was 0.992 for the 2nd degree polynomial equation (1)

$$C_p = 60.044 + 0.055T - 2.933 \cdot 10^{-5}T^2, \tag{1}$$

where T is the absolute temperature.

Since the experiments could be performed only up to 498 K, the value of C_p was extrapolated from Eq. (1) to the established melting point of $HgBr_2$ at 512 K (Fig. 1). Equation (1) was also used to calculate the entropy and enthalpy increments of mercury dibromide.

Universal formulas for the relationship between the isobaric heat capacity and the standard entropy are given in Ref. [8]. From the expressions of [8], we can arrive at Eq. (2), which takes into account the temperature intervals of the properties of $HgBr_2$ studied in this work,

$$S = S(298) + \int_{298}^{512} \frac{C_p}{T} dT - \int_{173}^{298} \frac{C_p}{T} dT, \tag{2}$$

where $S(298)$ is the total entropy under standard conditions.

Note that the value of the standard entropy for mercury dibromide at 298 K was borrowed from

Refs. [8, 9]. It is important to note here that Refs. [8, 9] provide an optimized value of $S(298)$ for $HgBr_2$, which is determined by combining several approaches and can be considered reliable. The combination of equations (1) and (2) allowed us to obtain the dependence $S = f(T)$ – Fig. 3, white circles. Our results confirmed the average values from Refs. [8, 9] (Fig. 3, white circles and red triangles). At the selected temperatures 300, 400 and 500 K, the maximum difference in S values did not exceed 0.1%.

The total enthalpy for mercury dibromide was determined similarly to Ref. [30]. The basic formulas from Refs. [8, 9, 31] were used. The calculated expression for $HgBr_2$ was (3)

$$H = H(298) + \int_{298}^{512} C_p dT - \int_{173}^{298} C_p dT. \tag{3}$$

According to classical thermochemical concepts [8], at standard pressure, the total enthalpy $H(298)$ is equal to the enthalpy of formation $\Delta Hf(298)$ of a compound. For $HgBr_2$, the National Bureau of Standards of USA [32] recommends the value $\Delta Hf(298) = -169.452$ kJ/mol (if 1 $J = 0.239$ Cal [15]). The combination of the recommended value [32] with equations (1) and (3) allowed us to build a dependence $H = f(T)$ – Fig. 4, white squares.

The determined values of S and H made it possible to calculate the total Gibbs energy G of the studied compound. For this purpose, we used the classical formula (4) [8]:

$$G = H - TS. \tag{4}$$

The resulting dependence $G = f(T)$ is shown in Fig. 4, white circles. It should be noted that our values of the standard enthalpy and Gibbs energy for $HgBr_2$ were compared only with the data of Ref. [8] (Fig. 4, two types of red crosses). This is because only Ref. [8] has direct values of H and G. At the same time, only indirect functions are given in Ref. [9]. Thus, at the base temperatures 300, 400 and 500 K, the maximum differences in the values of the standard functions (Fig. 4) did not exceed 0.2%.

The thermochemical properties of mercury dibromide were determined similarly to Ref. [30]. The basic principles of thermochemistry [8, 9, 31] were adapted to $HgBr_2$ in the form of expressions (5) and (6)
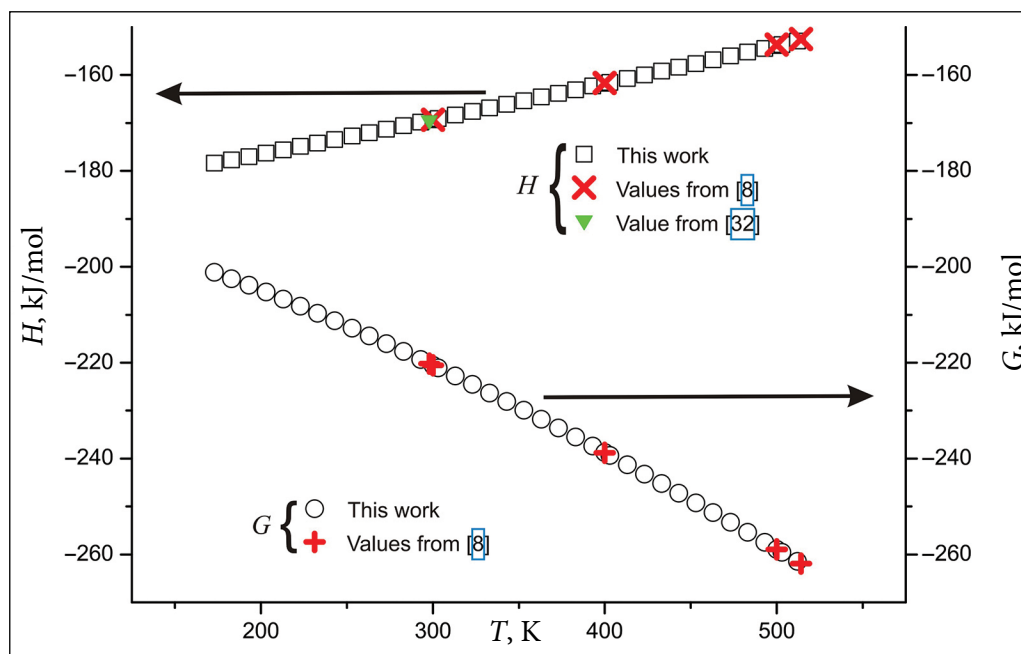
Fig. 4. Dependences of the standard enthalpy and the Gibbs energy on temperature for HgBr$_2$

$$\Delta Hf(\text{HgBr}_2) = \text{H}(\text{HgBr}_2) - \Sigma\{\text{H}(\text{Hg}) + \text{H}(\text{Br}_2)\}, \; (5)$$

$$\Delta Gf(\text{HgBr}_2) = \text{G}(\text{HgBr}_2) - \Sigma\{\text{G}(\text{Hg}) + \text{G}(\text{Br}_2)\}, \; (6)$$

where ΔHf and ΔGf are the enthalpy and Gibbs energy of formation, respectively.

In order to perform calculations according to formulas (5) and (7), we used our values of $H(\text{HgBr}_2)$ and $G(\text{HgBr}_2)$ at temperatures 173–293 and 303–512 K (Fig. 4). In turn, the values for the elemental components of Hg and Br$_2$ at 100–600 K were taken from Ref. [9]. Note that the total Gibbs energy was calculated from the function from Ref. [9]. It should be noted that the data in Ref. [9] had one drawback – the vast majority of them are given in large steps 100 K. In this regard, additional mathematical processing was performed to reduce the value step to 10 K. For this purpose, the temperature dependences of these functions were described by interpolation equations. The aggregate states of mercury and bromine were also taken into account. Thus, for Hg, two temperature intervals were taken: 100–234 K (solid mercury) and 234–600 K (liquid mercury). For Br$_2$, there were three intervals: 100–266 K (solid bromine), 266–333 K (liquid bromine) and 333–600 K (gaseous bromine). In total, ten polynomial equations were obtained for the elemental components. For most of them, high coefficients

of determination $R^2 = 0.996$–1.000 were achieved. The final dependences $\Delta Hf = f(T)$ and $\Delta Gf = f(T)$ for the interaction product Hg + Br$_2$ = HgBr$_2$ are shown in Fig. 5.

Our results were compared with the average values from Refs. [8, 9] (Fig. 5, two types of red crosses). Here, we note that the amounts of ΔHf and ΔGf for HgBr$_2$ are almost identical (with differences of up to 0.05%) in Refs. [8, 9]. The high consistency of the values in Refs. [8, 9] is explained by the mathematical processing of the same initial data.

At the selected temperatures 300, 400 and 500 K, the maximum difference between our ΔHf values and the average amounts from Refs. [8, 9] was close to 0.1%. At the same time, the values of ΔGf obtained in this work differed more strongly from the average data from Refs. [8, 9]: the maximum difference was about 0.6% (Fig. 5).

The abrupt increase in the negative values of $\Delta Hf(\text{HgBr}_2)$ at three temperatures 234, 266 and 333 K is noteworthy (Fig. 5). This is due to the phase transitions of the initial mercury and bromine [9]. These temperatures can be used to develop new efficient methods for the synthesis of mercury dibromide. The maximum jump in the enthalpy of formation of HgBr$_2$ from –170.40 to –199.95 kJ/mol occurs when heated by only one degree from 332 to 333 K (Fig. 5). Also, a rather high jump in the values of $\Delta Hf(\text{HgBr}_2)$ from
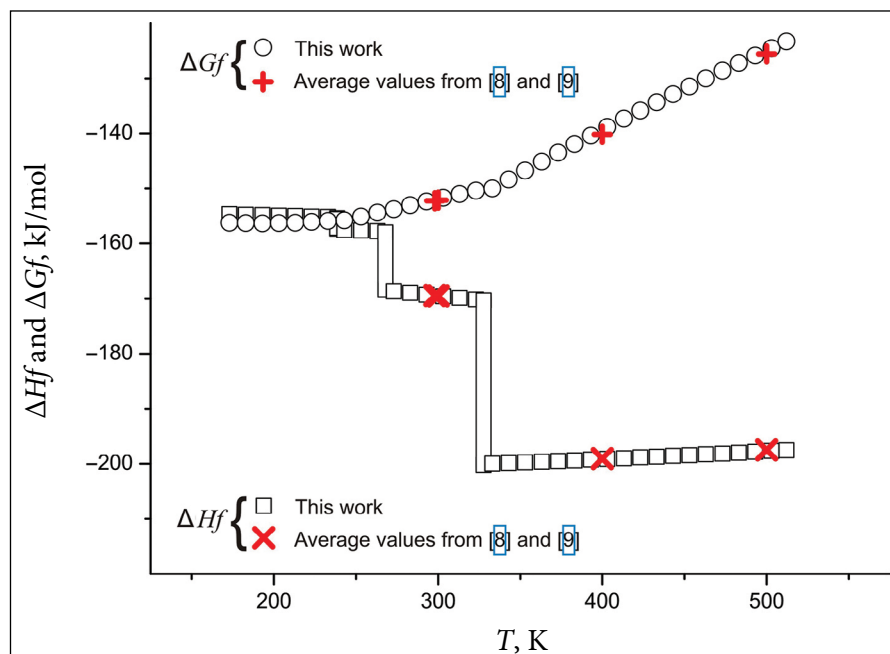
Fig. 5. Dependences of the enthalpy and the Gibbs energy of formation on temperature for HgBr$_2$

–157.74 to –168.45 kJ/mol is observed when moving from 265 to 266 K (Fig. 5). Probably, it is at temperatures 332–333 K or even 265–266 K that individual mercury dibromide can be obtained with the minimal energy consumption.

It should be noted that the change in the curve $\Delta Gf = f(T)$ for HgBr$_2$ at the phase transition temperatures of the initial elemental components is noticeable to a much lesser extent (Fig. 5). Consequently, $\Delta Gf(\text{HgBr}_2)$, unlike $\Delta Hf(\text{HgBr}_2)$, depends less on the physicochemical transformations of the initial Hg and Br$_2$.

Additional thermodynamic and thermophysical properties of HgBr$_2$

A more fundamental thermodynamic parameter than C_p is its isochoric counterpart C_V [33]. However, it is much more difficult to study the isochoric heat capacity. In the world scientific periodicals, we were unable to find direct methods for the experimental determination of C_V for solid compounds. Instead, semi-empirical approaches [22–25, 34] or indirect experiments [8, 33, 35] are used. Indirect methods are mainly based on formula (8) [8, 22, 35]

$$C_p - C_V = \alpha_V^2 VT/\beta_T \qquad (7)$$

or 8) [35]

$$C_p - C_V = \alpha_V^2 VTB^T, \qquad (8)$$

where α_V is the volume thermal expansion coefficient, V is the molar volume, β_T is the isothermal compressibility, and B^T is the isothermal bulk modulus.

Using indirect approaches to determine the isochoric heat capacity requires a lot of experimental data: C_p, α_V, V, β_T or B^T. The most difficult is to directly investigate the thermal expansion and compressibility of a solid compound. This requires sophisticated high-temperature X-ray equipment [36, 37].

In view of the above, a simplified approach was used in this work. The isochoric heat capacity of HgBr$_2$ at 298 K was estimated by the semi-empirical Magnus–Lindemann method [22–25, 34]. Note that the accuracy of this approach is not lower than some experimental and *ab initio* methods [23, 24]. The calculated expression at standard temperature was of the form (9)

$$C_V - C_p - 298^{3/2}x, \qquad (9)$$

where x is a certain coefficient [22, 38].

The method for determining x is given in Ref. [22]. Then, using Eq. (8) [23, 35], we obtained the value of the isothermal bulk modulus

$$B^T = C_V B^S/C_p, \qquad (10)$$

where B^S is the isentropic (adiabatic) bulk modulus.

In Eq. (10), we used our values of C_V and C_p, and the values of B^S were borrowed from Refs. [20, 21]. Here, we note that the elastic moduli [20, 21] are considered to be adiabatic parameters [39]. Therefore, B from Ref. [20], it was considered an isentropic or adiabatic modulus.

Then, using formula (8), we calculated the value of α_V. In this case, the molar volume of mercury dibromide was determined by the molar mass M and density d taken from the reference book [15]. Next, the value of the Grüneisen constant γ_G was obtained using expression (11) [22, 40, 41]:

$$\gamma_G = (C_p - C_V)/\alpha_V C_V T. \qquad (11)$$

Thus, $HgBr_2$ at 298 K has the following parameters: $B^T = 3.71$ GPa, $\beta_T = 0.27 \cdot 10^{-9}$ Pa, $\alpha_V = 3.50 \cdot 10^{-4}$ 1/K and $\gamma_G = 1.18$ (dimensionless value). These properties have been determined for the first time, so we cannot compare them with the data of other researchers. We only note that in terms of the order of thermal expansion (10^{-4} 1/K) of mercury dibromide is close to some alkali metal halides [42]. However, its value is higher. This can probably be explained by the low stability of mercury compounds: their Gibbs energy is less negative and their melting point is lower compared to alkali metal halides [8, 9, 15]. Accordingly, the crystal lattice of $HgBr_2$ is less stable and undergoes greater expansion due to thermal effects.

According to Grüneisen's law [43], at any temperature, the ratio of the coefficient of thermal expansion to the isobaric heat capacity is the same or almost the same:

$$\alpha_V/C_p \approx \text{const.} \qquad (12)$$

Based on this law [43] and formula (11) [22, 40, 41], the temperature dependences of α_V and C_V were calculated for mercury dibromide. It was assumed to be independent γ_G of T [40, 41], and for $HgBr_2$ $\alpha_V/C_p = 4.74 \cdot 10^{-6}$ mol/J (our result). The obtained dependences $\alpha_V = f(T)$ and $C_V = f(T)$ are shown in Figs. 6 and 7, respectively.

As can be seen from Fig. 6, the temperature dependence for mercury dibromide is close to linear (it can be described by a straight line equation with a high $R^2 = 0.994$). This result is in good agreement with classical ideas. According to Refs. [40, 44], in wide temperature intervals, the thermal expansion of solids follows a linear law.

The course of $C_V = f(T)$ curve for mercury dibromide (Fig. 7) does not contradict Debye's theory: when solid materials are heated, their isochoric heat capacity initially increases, and when certain temperatures are reached, it hardly changes [45]. However, for $HgBr_2$ at 413–512 K, a slight decrease (up to 0.8%) in its C_V was observed (Fig. 7). Similar features were recorded in other works [40, 46]. Thus, in Ref. [40], a decrease in the isochoric heat capacity of NaCl and Ag in
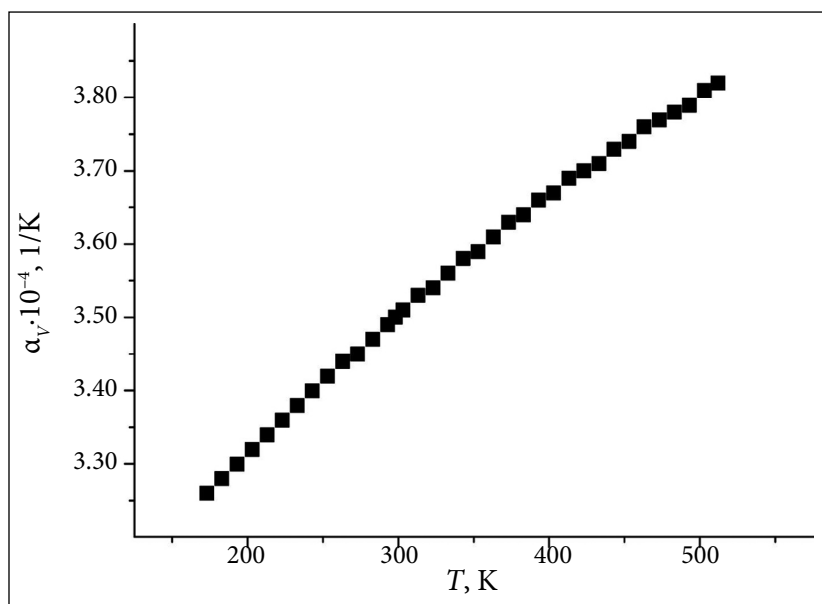

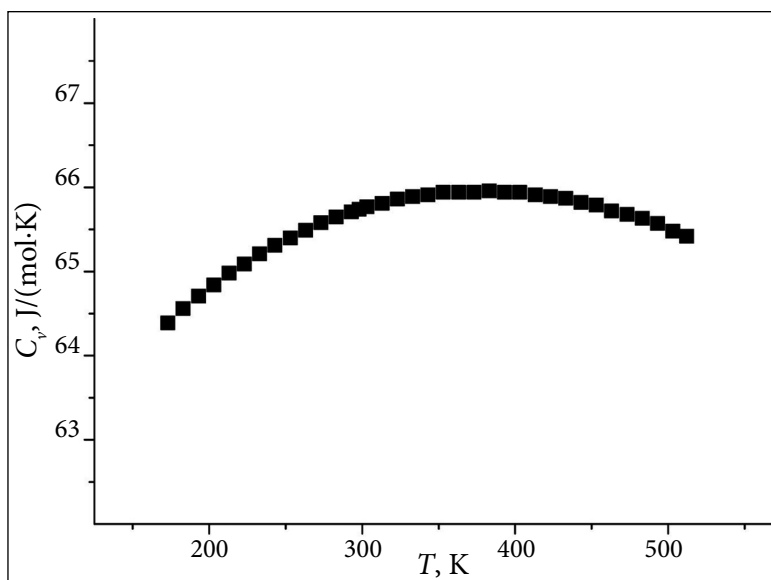**Fig. 6.** Dependence of the volume thermal expansion coefficient on temperature for $HgBr_2$

Fig. 7. Dependence of the isochoric heat capacity on temperature for HgBr$_2$

the high temperature region was mentioned. In Ref. [46], a slight decrease of C_V was observed when approaching the melting point of the studied compound Ni$_3$(PO$_4$)$_2$. In Ref. [40], referring to Eucken and Dannöhl, the effect of a decrease in the high-temperature isochoric heat capacity was explained by the peculiarities of the crystal lattice vibrations of the materials under study.

The availability of C_V(HgBr$_2$) values allowed us to calculate the corresponding amounts of the Debye temperature. For this purpose, we used the Debye function tables [47]. The constructed $\theta_D = f(T)$ dependence is shown in Fig. 8.

As can be seen in Fig. 8, heating mercury dibromide leads to a monotonic increase in its θ_D. Although the values of the isochoric heat capacity and the Debye temperature are closely interrelated [47], the peculiarities in the $C_V = f(T)$ dependence at 413–512 K (Fig. 7) did not affect the $\theta_D = f(T)$ curve – no clearly defined anomalies are observed (Fig. 8).

The isochoric heat capacity is also closely related to the phonon thermal conductivity (13) [33, 45, 48]

$$k = C_V \bar{l}\bar{v}/3, \qquad (13)$$

where $\bar{l}$ is the phonon mean free path, $\bar{v}$ is the average phonon velocity [33] or the average sound velocity [45].

In turn, $\bar{v}$ can be determined from expression (14) [49]

$$\bar{v} = \left\{(1/3)\left(\left(2/v_s^3\right) + 1/v_l^3\right)\right\}^{-1/3}, \qquad (14)$$

where v_s is the shear or transverse phonon velocity, and v_l is the longitudinal phonon velocity.

The phonon velocities are determined by Navier's equations (15) and (16) [39, 49–51]

$$v_s^2 = G_{sh}/d, \qquad (15)$$

$$v_l^2 = (3B^s + 4G_{sh})/3d, \qquad (16)$$

where G_{sh} is the shear modulus.

In this work, the values of G_{sh}(HgBr$_2$) and B^s(HgBr$_2$) were borrowed from Refs. [20, 21], and d(HgBr$_2$) from [15]. The phonon mean free path length was estimated similarly to Ref. [52]. According to expressions (14)–(16), the following values were obtained for mercury dibromide: v_l =1106 m/s, v_s =632 m/s and $\bar{v}$ =702 m/s. Note that experimental amounts of sound velocities for HgBr$_2$ are not available in the literature. However, there is information on the value of the transverse wave velocity for mercury monobromide HgBr, another compound of the Hg–Br$_2$ system, which is close to 300 m/s [53]. As you can see, the order of the values of v_s(HgBr$_2$) and v_s(HgBr) is the same.

By formula (13), we obtained k(HgBr$_2$) = 0.19 W/K·m at 298 K. According to Ref. [52], samples with k < 0.6 W/K·m are promising low-thermal conductive materials, which obviously include mercury dibromide.
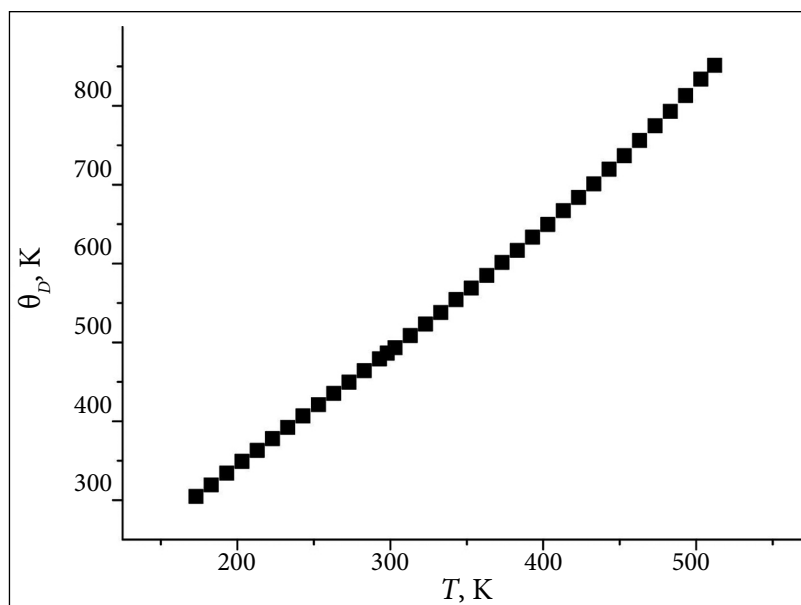
Fig. 8. Dependence of the Debye temperature on the absolute temperature for HgBr$_2$

Thus, the determined properties expand the information about the physical and physicochemical parameters of mercury dibromide, can be used to develop more efficient methods of its synthesis, are important for the selection of optimal modes of use HgBr$_2$ in various devices, can open up new perspectives for practical applications and will be valuable for further studies of this compound.

CONCLUSIONS

For the first time, the valid isobaric heat capacity of mercury dibromide HgBr$_2$ (a promising material for laser technologies) was investigated by direct measurement at temperatures 173–512 K. In the range 298–512 K, the results obtained with a difference of 1–2% confirmed the fitting method used in previously published works. For the first time, the basic thermodynamic and thermochemical functions of HgBr$_2$ in the low-temperature range 173–298 K were determined. For the first time, by combining experimental values, semi-empirical methods and *ab initio* calculations taken from the literature, we have obtained values for a number of additional thermodynamic and thermophysical properties of crystalline mercury dibromide: isothermal compressibility (isothermal bulk modulus), phonon velocities and phonon thermal conductivity (under standard conditions); Grüneisen's constant, volume thermal expansion, isochoric heat capacity

and Debye temperature (in the temperature range 173–512 K). Among the determined properties, the most promising ones include high rates of volume thermal expansion coefficients (3.3–3.8)·10^{-4} 1/K in the range 173–512 K and a low phonon thermal conductivity ~0.2 W/K·m at 298 K.

References

1. A. Malinina, *Optical Characteristics of Gas-Dicharge Plasma in Mixtures of Mercury Dibromide Vapor with Gases*, Cambridge Scholars Publishing (2020).
2. A. N. Malinin, K. B. Molnar, A. O. Malinina, *Sci. Herald Uzhhorod Univ. Ser. Phys.*, **(50)**, 9 (2021).
3. M. M. Guivan, A. A. Malinina, A. Brablec, *J. Phys. D Appl. Phys.*, **44(22)**, 224012 (2011).
4. A. A. Malinina, A. N. Malinin, A. K. Shuaibov, *Open Phys. J.*, **(4)**, 43 (2018).
5. T. Liu, J. Qin, G. Zhang, et al., *Appl. Phys. Lett.*, **93**, 091102 (2008).
6. Q. Yuan, X. Liu, Y. Xiao, T. Wang, J. Wang, Y. Zhang, *J. Environ. Chem. Eng.*, **11(3),** 109622 (2023).
7. M. Yu, G. Luo, R. Sun, R. Zou, X. Li, H. Yao, *Chem. Eng. J.*, **406**, 127010 (2021).
8. I. Barin, *Thermochemical Data of Pure Substances*, John Wiley & Sons, Weinheim (1995).
9. M. W. Chase Jr., *NIST-JANAF Thermochemical Tables*, 4th edn., Journal of Physical and Chemical Reference Data, Monograph 9, American Institute of Physics (1998).

10. G. J. Janz, J. Goodkin, *J. Phys. Chem.*, **63**, 1975 (1959).

11. M. Guinchant, *Comp. Rend.*, **149**, 479 (1909).

12. Yu. V. Minets, Yu. V. Voroshilov, V. V. Pan'ko, V. A. Khudolii, *J. Alloys Compd.*, **365(1–2)**, 121 (2004).

13. I. Ye. Barchii, Ye. Yu. Peresh, V. M. Rizak, V. O. Khudolii, *Heterohenni rivnovahy: Navchalnyi posibnyk (Heterogeneous Equilibria: A Study Guide)*, Zakarpattia, Uzhhorod (2003).

14. M. Hostettler, D. Schwarzenbach, *C. R. Chim.*, **8**, 147 (2005).

15. D. R. Lide (ed.), *Handbook of Chemistry and Physics*, 84th edn., CRC Press (2003–2004).

16. H. Braekken, *Z. Kristallogr.*, **81(1–6)**, 152 (1932).

17. H. J. Verweel, J. M. Bijvoet, *Z. Kristallogr.*, **77(1–6)**, 122 (1931).

18. G. Nolze, W. Kraus, *Powder Diffr.*, **13(4)**, 255 (1998).

19. T. J. B. Holland, S. A. T. Redfern, *J. Appl. Cryst.*, **30(1)**, 84 (1997).

20. *ELATE: Elastic Tensor Analysis* [https://progs.coudert.name/elate/mp?query=mp-23292].

21. R. Gaillac, Pl. Pullumbi, Fr.-X. Coudert, *J. Phys. Condens. Matter*, **28**, 275201 (2016).

22. A. Kozma, *Grail of Science*, **(26)**, 196 (2023), and references cited therein.

23. A. Kozma, *Technol. Transfer Fundam. Princip. Innov. Tech. Solutions*, **4**, 14 (2020), and references cited therein.

24. A. A. Kozma, *Int. J. Educ. Sci.*, **2(2)**, 22 (2019).

25. F. S. Ibrahimova, *Chem. Problems*, **3(17)**, 358 (2019).

26. K. Popa, R. J. M. Konings, *Thermochim. Acta*, **445**, 49 (2006).

27. A. L. Smith, J.-C. Griveau, E. Colineau, P. E. Raison, R. J. M. Konings, *Thermochim. Acta*, **617**, 129 (2015).

28. C. G. Maier, K. K. Kelley, *J. Amer. Chem. Soc.*, **54**, 3243 (1932).

29. J. O. Rawlings, S. G. Pantula, D. A. Dickey, *Applied Regression Analysis: A Research Tool*, 2nd edn., Springer-Verlag, New York (1998).

30. A. Kozma, N. Golub., Ye. Golub, et al., *Chemija*, **34(1)**, 19 (2023).

31. *Thermodynamic Data Bases* [https:/en.wikipedia.org/wiki/Thermodynamic_data_bases_for_pure_substances].

32. F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, I. Jaffe, *United States National Bureau of Standards, Circular 500: Selected Values of Chemical Thermodynamic Properties*, United States Government Printing Office, Washington, D. C. (1952).

33. C. Kittel, *Introduction to Solid State Physics*, 4th edn., John Wiley & Sons, New York, London, Sydney, Toronto (1971).

34. A. A. Kozma, Ye. Yu. Peresh, I. Ye. Barchij, M. Yu. Sabov, O. S. Glukh, V. V. Tsygyka, *Sci. Bull. Uzhh. Univ. Ser. Chem.*, **2(22)**, 87 (2009).

35. W. P. Mason (ed.), *Physical Acoustics: Principles and Methods. Vol. 1 – Part A: Method and Devices*, Academic Press, New York and London (1964).

36. A. Taylor, N. J. Doyle, *J. Appl. Crystallogr.*, **4**, 103 (1971).

37. A. Taylor, N. J. Doyle, *J. Appl. Crystallogr.*, **4**, 109 (1971).

38. E. Schrödinger, *Phys. Z.*, **20**, 452 (1919).

39. W. P. Mason (ed.), *Physical Acoustics: Principles and Methods. Vol. IV – Part B: Applications to Quantum and Solid State Physics*, Academic Press, New York and London (1968).

40. F. Seitz, *The Modern Theory of Solids*, McGraw-Hill, New York and London (1940).

41. I. Licea, A. Ioanid, *Phys. Status Solidi B*, **212**, 27 (1999).

42. Zh.-H. Fang, *Phys. B*, **357**, 433 (2005).

43. E. Grüneisen, *Ann. Phys.*, **331(6)**, 211 (1908).

44. A. Eucken, W. Dannöhl, *Z. Elektrochem.*, **40(11)**, 814 (1934).

45. J. Pei, H. Li, H.-L. Zhuang, et al., *InfoMat*, **4(12)**, e12372 (2022).

46. A. A. Kozma, N. P. Golub, E. O. Golub, N. B. Vashkeba, V. V. Stehura, V. I. Gomonaj, *Nauk. vìsn. Užgorod. unìv., Ser. Hìm.*, **2(40)**, 52 (2018).

47. J. E. Kilpatrick, R. H. Sherman, *Six-place Tables of the Debye Functions $(E-E_0)/3RT$, $C_V/3R$, and $S/3R$*, Scientific Laboratory of the University of California, Los Alamos (1964).

48. C. Kittel, *Introduction to Solid State Physics*, 8th edn., Wiley (2005).

49. W. P. Mason (ed.), *Physical Acoustics: Principles and Methods. Vol. III – Part B: Lattice Dynamics*, Academic Press, New York and London (1965).

50. Y. O. Ciftci, Y. Ünlü, K. Colakoglu, E. Deligoz, *Phys. Scr.*, **80**, 025601 (2009).

51. E. Screiber, O. L. Anderson, N. Soga, *Elastic Constants and Their Measurements*, McGraw-Hill, New York (1973).

52. K. Kurosaki, H. Uneda, H. Muta, Sh. Yamanaka, *J. Alloys Compd.*, **376**, 43 (2004).

53. N. B. Singh, M. Gottlieb, G. B. Brandt, A. M. Stewart, R. Mazelsky, M. E. Glicksman, *J. Cryst. Growth*, **137**, 155 (1994).

Anton Kozma, Antonina Malinina, Evgeniy Golub, Vasylyna Rusyn, Nelya Golub, Vitalii Dziamko, Viktoriia Dziamko, Oleksandr Malinin, Andrii Solomon

HgBr$_2$ TERMODINAMINĖS, TERMOCHEMINĖS IR TERMOFIZIKINĖS SAVYBĖS

S a n t r a u k a

Kristalinio gyvsidabrio dibromido HgBr$_2$ (perspektyvios medžiagos lazerinėms technologijoms) galiojanti izobarinė šiluminė talpa ištirta tiesiogiai matuojant 173–512 K temperatūroje. Nustatytos jo pagrindinės termodinaminės ir termocheminės funkcijos šiomis sąlygomis. Gautos kelių papildomų HgBr$_2$ termodinaminių ir termofizikinių savybių vertės: izoterminio suspaudžiamumo (izoterminio tūrinio modulio), fononų greičių, fononų šiluminio laidumo (standartinėmis sąlygomis), Grüneizeno konstantos, tūrio šiluminio plėtimosi, izochorinės šiluminės talpos, Debye'aus temperatūros (173–512 K temperatūrų intervale).