Caloric properties of Cs\textsubscript{60}Bi\textsubscript{40} alloy in the temperature range of 293-1125 K

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Abstract. The results of the enthalpy measurements of the Cs\textsubscript{60}Bi\textsubscript{40} alloy in the range of 431–1127 K of the solid and liquid states are presented. The experiments were carried out by the mixing method on a massive isoperibolic calorimeter. The estimated errors for enthalpy and heat capacity of the melt were 0.4 and 1.4%, respectively. It was shown that the heat capacity of the melt decreases linearly with increasing temperature, and its absolute value in the studied temperature range is 1.25–1.45 times higher than the additive value. Table of recommended values of caloric properties over the range from 298.15 K to 1175 K was developed.

1. Introduction
Liquid alloys of alkali metals with bismuth and lead belong to a rather rare class of systems in which, along with the metallic nature of the interatomic interaction, the formation of associates with ionic bonds is assumed. The base for this is the presence of extrema on the concentration dependences of the electrical resistance [1] and thermal expansion coefficient [2], which lie in the region of 25 at. % bismuth and 50 at. % lead. However, there have no studies of the caloric properties of melts of heavy alkali metal with bismuth, with the exception of our works [3, 4]. To confirm the absence of anomalies in the heat capacity and enthalpy of mixing in the region of 50 at. % of bismuth, it is necessary to have experimental data in the interval adjacent to the equiatomic composition; therefore, the aim of this work was to measure the caloric properties of the Cs\textsubscript{60}Bi\textsubscript{40} liquid alloy in a wide temperature range of the condensed state.

2. Experimental details
The experiments were carried out on a massive calorimeter using a sealed stainless steel ampoule. The sample temperature was measured by a thermocouple (type S), which was introduced directly into the ampoule in a protective sleeve. The design of the calorimeter, as well as the measuring procedure and results processing were described in [5, 6]. A sample of Cs\textsubscript{60}Bi\textsubscript{40} alloy was prepared from components with a purity of 99.94 wt. % (Cs) and 99.98 wt. % (Bi). All operations for the preparation of the alloy and the sealing of the ampoule (arc welding) were carried out in a glove box with an argon atmosphere of 99.992% purity. The chemical composition was determined by the gravimetric method and amounted to $X_{Cs} = 60.0 \pm 0.01$ at. %, at the sample mass of 32.170 g. The calculated molecular weight of the alloy was 163.338 g mol$^{-1}$. 
3. Results and Discussion

Before the main measurements, differential thermal analysis of the alloy sample which was placed into the prepared ampoule was carried out. Experiments have shown the existence of only one thermal effect at a liquidus temperature:

\[ T_L = 794.9 \pm 1.5 \text{ K} \]  

Prior to crystallization, the melt was supercooled by 1.2–2.9 K, and the value (1) was reproduced within 0.6 K. The obtained value within the estimated error coincided with the data [2], where it was found that \( T_L = 796.7 \pm 1.5 \text{ K} \). In this work, by scanning of the Cs\(_{60}\)Bi\(_{40}\) melt by a gamma-ray beam, the homogeneity of the sample was controlled and the conditions for its achievement were determined. The equality of liquidus temperatures (1) and [2] indirectly confirms the absence of concentration gradients in the Cs\(_{60}\)Bi\(_{40}\) liquid alloy in our work and, therefore, indicates the correct choice of method for preparing the measuring cell before dropping into the calorimetric unit.

Enthalpy (\( H \)) was measured in the temperature range of 431–1126 K. Twelve points were obtained for the solid state (431-748 K) and 18 points for the melt (807-1126 K). The obtained data were recalculated based on the standard temperature of 298.15 K (table 1, figure 1) using the procedure described in [7]: \( H_{298}(T) = H(T) - H(298.15) \), and were approximated by least squares method. The choice of the type of analytical dependence for approximation of the measurement results in the mixing method is important for determining the heat capacity (\( C_p \)), since \( C_p \) is found by differentiating the temperature dependence of \( H_{298}(T) \), and is not measured directly. To solve this problem, we considered the temperature dependence of the "experimental" heat capacity, which was determined directly from the measured enthalpy values. The calculation was carried out using the expression [6]:

\[ C_p(T_j) = \frac{H_{298}^{i+1} - H_{298}^{i-1}}{T_{i+1} - T_{i-1}}, \]  

where \( i \) is the number of the experimental point for the single-phase region, \( T_j = \frac{T_{i+1} + T_{i-1}}{2} \). Due to high sensitivity of the "experimental" heat capacity to even insignificant errors in the enthalpy increment, the points giving the "ejections" of \( C_p \), were not taken into account in the calculation, and a number of points of those obtained practically at the same temperatures were excluded as well. For the solid phase, the point \( H_{298}(298.15) \) K = 0 was added.

Analysis of the obtained data (figure 1) has shown that the temperature dependence of the "experimental" heat capacity of the Cs\(_{60}\)Bi\(_{40}\) solid alloy is well described by the power polynomial of the third degree; the first-degree polynomial works well for the melt. Considering this, the initial data on the enthalpy increment were approximated by polynomials of the fourth and second degree, respectively.

For solid state:

\[ H_{298}(t) = 26.44 t + 1.307 \times 10^2 t^2 - 5.006 \times 10^4 t^3 + 7.885 \times 10^8 t^4, \]  

where \( H_{298} \) in J mol\(^{-1}\), \( t = T - 298.15 \), \( T \) in K. The average absolute deviation of points from equation (3) is 15.4 J mol\(^{-1}\) or 0.20 % (figure 2). For the liquid state:

\[ H_{298}(t_1) = 23435 + 42.46 t_1 - 5.43 \times 10^3 t_1^2, \]  

where \( t_1 = T - 794.9 \) K, the average absolute deviation of points from equation (4) is 22.5 J mol\(^{-1}\) or 0.075 %. The enthalpy change at melting determined using equations (3) and (4) is:

\[ \Delta H_{SL} = 8412 \pm 200 \text{ J mol}^{-1}, \]  

where the error is determined through the confidence limits (95%) of the approximation error of the enthalpy at the melting temperature for solid 190 J mol\(^{-1}\) and liquid phases 45 J mol\(^{-1}\).
### Table 1. Experimental enthalpy of the Cs₆₀Bi₄₀ alloy.

| T (K) | H₂₉₈ (J mol⁻¹) | T (K) | H₂₉₈ (J mol⁻¹) |
|-------|----------------|-------|----------------|
| 431.0 | 3647           | 852.2 | 25842          |
| 450.7 | 4193           | 877.1 | 26857          |
| 470.6 | 4750           | 901.8 | 27897          |
| 490.3 | 5320           | 901.9 | 27861          |
| 510.1 | 5889           | 926.7 | 28912          |
| 529.9 | 7018           | 951.6 | 29946          |
| 549.9 | 8391           | 976.4 | 30982          |
| 599.5 | 9914           | 1001.3| 31984          |
| 649.2 | 11541          | 1026.3| 33000          |
| 698.7 | 12494          | 1051.3| 33969          |
| 728.4 | 13211          | 1076.3| 34996          |
| 748.1 | 23975          | 1076.5| 34978          |
| 807.5 | 24826          | 1126.5| 36883          |
| 827.4 | 24858          | 1126.6| 36896          |

### Figure 1. Enthalpy and heat capacity temperature dependences of Cs₆₀Bi₄₀ alloy in the solid (AS) and liquid (LB) states.
1, 4 – experimental values of $H_{298}$ and $C_p$, respectively; 2, 3 – calculation of enthalpy and heat capacity according to equations (3), (4).
Figure 2. Deviations of experimental enthalpy of the solid (triangles) and liquid (circles) Cs₆₀Bi₄₀ alloy from equation (3) and (4), respectively. \( \delta H_{298} = (H_i - H_{app}) \times 100\% \). 

\( H_i \) and \( H_{app} \) — measured and smoothed values of enthalpy.

Table 2. Recommended values of caloric properties of Cs₆₀Bi₄₀ alloy.

| Phase  | \( T \) (K) | \( H_{298} \) (kJ mol⁻¹) | \( C_p \) (J mol⁻¹ K⁻¹) |
|--------|-------------|--------------------------|-------------------------|
| Solid  | 298.15      | 0.00                     | 26.44                   |
|        | 300         | 0.05                     | 26.49                   |
|        | 350         | 1.40                     | 27.43                   |
|        | 400         | 2.78                     | 27.88                   |
|        | 450         | 4.18                     | 28.05                   |
|        | 500         | 5.59                     | 28.19                   |
|        | 550         | 7.00                     | 28.53                   |
|        | 600         | 8.45                     | 29.32                   |
|        | 650         | 9.95                     | 30.78                   |
|        | 700         | 11.54                    | 33.16                   |
|        | 750         | 13.28                    | 36.69                   |
|        | \( T_L = 794.9 \) | 15.02                    | 41.03                   |
|        | \( T_L = 794.9 \) | 23.44                    | 42.46                   |
|        | 800         | 23.65                    | 42.41                   |
|        | 850         | 25.76                    | 41.86                   |
|        | 900         | 27.84                    | 41.32                   |
| Melt   | 950         | 29.89                    | 40.78                   |
|        | 1000        | 31.92                    | 40.23                   |
|        | 1050        | 33.91                    | 39.69                   |
|        | 1100        | 35.88                    | 39.15                   |
|        | 1125        | 36.86                    | 38.87                   |
Table 3 shows the recommended values of the enthalpy increment and heat capacity of the Cs$_{60}$Bi$_{40}$ alloy in the solid and liquid states calculated according to equations (2) and (3). The errors of $H_{298}$ and $C_p$ for the melt are estimated as 0.4% and 1.4%, respectively. The error in the heat capacity of the solid alloy up to 750 K does not exceed 2.5% and increases up to 5-7% due to extrapolation to the liquidus temperature.

The relative deviations of experimental values of enthalpy and heat capacity of the Cs$_{60}$Bi$_{40}$ alloy in the liquid state from their additive value reaches 22% and 47%, respectively. A significant excess of the values of caloric properties compared over calculations according to the laws for ideal solutions indirectly confirms the assumption that there are complexes in the melt with an ionic character of the interatomic interaction.

**Conclusion**

Caloric properties of the cesium-bismuth system alloy with the bismuth content of 40 at. % in a wide temperature range of the condensed state have been investigated for the first time. The enthalpy change on melting has been determined; the heat capacity of the Cs$_{60}$Bi$_{40}$ liquid alloy is shown to decrease linearly with increasing temperature. Significant deviations of the caloric properties of the melt from additive values indicate the presence of associates with ionic bonds in it.

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