Heat capacity of liquid Cs$_{80}$Bi$_{20}$ alloy with a partly ionic character of interatomic interaction

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Abstract. Enthalpy increment of Cs$_{80}$Bi$_{20}$ liquid alloy in the temperature range of 857–1076 K was measured by mixing method on a massive calorimeter with an isothermal shell. The heat capacity of the melt was determined and it was found that for the studied temperature range it remains constant, and its absolute value exceeds significantly the calculation by the additivity rule. The estimated errors for enthalpy and heat capacity of the melt were 0.4 and 1%, respectively. An approximation equation was obtained for the dependence of the mass heat capacity of the solid alloys of the cesium-bismuth system at 298.15 K by the atomic concentration of bismuth.

1. Introduction
The concentration dependences of the electrical resistance [1] and thermal properties [2] of liquid alloys of the cesium-bismuth system revealed extrema in the region of 25 at. % Bi, and this is associated with the formation of associates with a partially ionic character of the interatomic interaction. Our measurements of the caloric properties of Cs-Bi melts also showed a significant excess of the specific heat of the Cs$_{72.9}$Bi$_{27.1}$ melt [3] over calculations according to the laws of ideal solutions. To determine the extent and shape of this maximum, it is necessary to perform measurements in a certain concentration range near 25 at. % Bi. In this connection, the goal of this work was to measure the enthalpy of the Cs$_{80}$Bi$_{20}$ alloy in a wide temperature range of the liquid state.

2. Experimental details
An isoperibolic drop calorimeter [4] and a sealed ampoule made of 12Kh18N10T stainless steel were used. The alloy components had a purity of 99.94 wt. % (Cs) and 99.98 wt. % (Bi). Sample preparation included purification of the initial materials from oxides (cesium was purified by filtering the melt through a metal filter, and bismuth was purified mechanically), filling the ampoule with Cs and Bi by the required masses, and sealing the ampoule with the sample by arc welding. All procedures were performed in a glove box with an atmosphere of pure argon. The chemical composition was determined by the gravimetric method and amounted to $X_{Cs} = 80.0 \pm 0.01$ at. %, the molecular weight of the alloy was 148.116 g mol$^{-1}$. The full measurement cycle included [4, 5] calibration of the calorimetric unit to determine its heat equivalent and heat transfer coefficient, as well as measuring the enthalpy of an empty ampoule and an ampoule with a sample (cell) in a given temperature range. The temperature was measured by S-type immersion thermocouple, which was verified by the solidification points of tin, lead, aluminum and copper directly in the installation. Based on these results, amendments were made to its readings.
Much attention was paid to achieving homogeneity of the investigated liquid sample. For this purpose, at the first stage, the cell was repeatedly melted sequentially up and down by “legs”, and before dropping it was preliminarily kept for 2 hours at 1100 K. The necessary time for melt homogenization was determined by the results of studies of the mutual diffusion coefficient in the Cs-Bi liquid system by the gamma method [6] and confirmed by reproducibility of the results of enthalpy measurements.

The developed technique for measuring enthalpy allows dropping an ampoule at an arbitrary temperature of the calorimetric body [4, 5]. In order to recalculate the enthalpy to a standard temperature of 298.15 K, in this case it is necessary to know specific heat of the sample under study at room temperature. We were not able to find such data in the literature, and it was not possible to apply the approach developed for such a case [7] because according to the phase diagram [8], the solidification of the Cs80Bi20 alloy completes beyond the working range of the calorimeter at the temperature of 301.55 K. For this reason, the concentration dependence of the isobaric heat capacity \( c_p(298.15 \text{ K}) \), obtained in our previous experiments with the cesium-bismuth system for other compositions, was considered. It turned out that the mass \( c_p(298.15 \text{ K}) \) changes quite regularly with temperature (Fig. 1). The approximation of the primary data gave the equation:

\[
c_p(298.15 \text{ K}) = 0.2424 - 3.442\times10^{-3} X + 4.337\times10^{-5} X^2 - 2.077\times10^{-7} X^3,
\]

where \( c_p(298.15 \text{ K}) \) in J(\(g\) K\(^{-1}\)), \( X \) is atomic percent of bismuth. The standard deviation of the experimental points from (1) is 0.004 J(\( g\) K\(^{-1}\)). The heat capacity of the Cs80Bi20 solid alloy estimated by (1) at 298.15 K is 0.1893 J(\( g\) K\(^{-1}\)). This value was used to recalculate the enthalpy to a standard temperature.

![Figure 1. Heat capacity of solid Cs-Bi alloys at 298.15 K. 1 – experimental values; 2 – equation (1); 3 – law for an ideal solution.](image-url)
3. Results and Discussion

The temperature of Cs$_{80}$Bi$_{20}$ alloy crystallization start, determined on the prepared measuring cell by the DTA method, was

$$T_L = 834 \pm 3 \text{ K}$$  \hspace{1cm} (2)

This value coincides with $T_L = 834 \pm 1.5 \text{ K}$ obtained in [2] by the gamma method under conditions of direct control of sample homogeneity, which indirectly confirms the absence of a concentration gradient in the melt in our work.

In the measurements, 7 experimental points were obtained in the temperature range of 857–1076 K of the liquid state. The enthalpy increments $H_{298}(T) = H(T) - H(298.15)$ are given in Table 1. Analysis of the initial data showed that they are well described by linear temperature dependence. The least squares method yields the equation:

$$H_{298}(t) = 23925 + 37.08 \ t, \hspace{1cm} (3)$$

where $t = T - 834 \ \text{K}$, $H_{298}$ in J mol$^{-1}$. The standard deviation of the points from the approximation dependence is 19.5 J mol$^{-1}$ or 0.065 % (Figure 2). The total error of enthalpy is estimated at 0.4% or 120 J mol$^{-1}$, and the heat capacity at 1%.

| $T$ (K) | $H_{298}$ (J mol$^{-1}$) | $T$ (K) | $H_{298}$ (J mol$^{-1}$) |
|--------|-------------------------|--------|-------------------------|
| 857.0  | 24783                   | 1021.2 | 30846                   |
| 911.6  | 26789                   | 1076.3 | 32897                   |
| 966.5  | 28862                   | 1076.3 | 32932                   |
| 1021.0 | 30860                   |        |                         |

**Table 1.** Experimental enthalpy of the Cs$_{80}$Bi$_{20}$ alloy.

![Figure 2](image-url)  

*Figure 2.* Deviations of the measured values of the enthalpy increment of Cs$_{80}$Bi$_{20}$ melt from the approximation equation (1) and the specific heat from calculations by the additivity rule, $\delta C_p = [C_{p,exp} / C_{p,add} - 1] \times 100\%$. 

1.

2.
Figure 2 also shows the relative deviations of the experimental heat capacity of the Cs$_{80}$Bi$_{20}$ liquid alloy from the calculation of $C_p$ according to the laws for ideal solutions. It is seen that the deviation of the specific heat decreases with increasing temperature, which can be explained by the decomposition of complexes with a partially ionic character of interatomic interaction. At the same time, the absolute value of $\delta C_p$ is significantly less than that for the Cs$_{72.9}$Bi$_{27.1}$ alloy, where it reaches 55% [3]. This indicates a sharp decrease in the probability of formation of associates with an ionic bond with a decrease in the concentration of bismuth below 25 at. %

Conclusions
For the first time experimental data were obtained on the enthalpy increment and heat capacity of the Cs$_{80}$Bi$_{20}$ melt at overheating above the liquidus temperature of up to 242 K. It was shown that the heat capacity of the liquid alloy remains constant in the studied temperature range. The deviation of the measured heat capacity from the calculations according to the laws for ideal solutions for the melt $\delta C_p(L)$ and solid alloy at 298.15 K have different signs, and the large positive values of $\delta C_p(L)$ confirm the existing assumption that there are associates with ionic bonds in the melt.

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