Enthalpy and heat capacity of Cs\(_{72.9}\)Bi\(_{27.1}\) alloy with a partly ionic character of interatomic interaction in the condensed state

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Abstract. The enthalpy of solid and liquid Cs\(_{72.9}\)Bi\(_{27.1}\) alloy was measured by a mixing method on a massive isothermal drop calorimeter in the temperature range of 432–1177 K. Approximation equations were obtained. The isobaric heat capacity and enthalpy change on melting were determined. The estimated errors for enthalpy and heat capacity were 0.5 and 1.5%, respectively. A significant positive deviation of the caloric properties from the additivity values was established. Tables of recommended values of caloric properties over the range from 298.15 K to 1175 K were developed.

1. Introduction
Cesium – bismuth alloys belong to a unique and poorly studied class of materials, which in the liquid state tend to form associates with a partly ionic character of interatomic interaction. This leads to significant deviations of the melts properties from their calculations according to the laws for ideal solutions, and the concentration dependences of properties have extremaums at some compositions [1-3]. A review of the published works showed the absence of reliable experimental data on the enthalpy and heat capacity of alloys of the cesium-bismuth system in a condensed state. At the same time, the caloric properties make it possible to estimate the energy interaction of components in solutions, therefore the aim of this work was to measure the enthalpy of an alloy of the cesium-bismuth system in solid and liquid states and to determine its temperature dependence of heat capacity.

2. Experimental details
The enthalpy \((H)\) of Cs\(_{72.9}\)Bi\(_{27.1}\) alloy was measured using a massive isothermal drop calorimeter, the design of which and data processing were described in [4]. All experiments were performed in an argon atmosphere with a purity of 99.992 vol. %. The sample temperature was measured by a thermocouple (type S), introduced directly into the ampoule in a protective sleeve. The thermocouple was tested by the solidification points of pure tin (99.99%), lead (99.99%), aluminum (99.99%) and copper (99.999%) directly in the installation under conditions identical to the main experiment.

The full measurement cycle included the calibration of the calorimetric unit to determine its thermal equivalent and heat transfer coefficient; measuring the enthalpy of an empty ampoule and the main experiment with a sample loaded into the ampoule. In all three cases, the temperature rise of the calorimetric unit was measured identically.
Approbation of the setup was carried out in experiments (573–1273 K) with sapphire [4]. Comparison of our results with recommendations [5] showed that the deviation for the enthalpy does not exceed 0.05%, and for the heat capacity it is 0.16%.

Sample of Cs\textsubscript{72.9}Bi\textsubscript{27.1} alloy was prepared from components with a purity of 99.94 wt. % (Cs) and 99.98 wt. % (Bi). Because of the high chemical activity of cesium, all operations for the preparation of the alloy and sealing the ampoule (arc welding) were carried out in a glove box with an argon atmosphere of 99.992% purity. The composition of alloy was determined by the gravimetric method and was equal to \( X_{\text{Cs}} = 72.9 \pm 0.005 \) at. % when the sample mass was 23.918 g. The calculated molecular mass of the alloy was 153.521 g mol\(^{-1}\). Calibration of the empty ampoule with a mass of 41.347 g was carried out under conditions identical to those of the basic experiments with alloy.

### 3. Results and Discussion

Before each measurement of the liquid alloy enthalpy, the sample was maintained at a constant temperature of at least 1 hour for melt homogenization [6]. Thermal analysis of Cs\textsubscript{72.9}Bi\textsubscript{27.1} showed the presence of one thermal effect at liquidus temperature, which amounted to \( T_L = 927.3 \) K ± 1.5 K. This value was reproduced within 0.02 K. Undercooling did not exceed (0.07–0.4 K). We were unable to find in the literature data on the heat capacity of alloys of the cesium – bismuth system in the range of room temperature. For this reason, to transform the measurement results to 298.15 K, an iterative procedure was applied [6].

The molar increment of the enthalpy \( H_{298} = H(T) - H(298.15) \) (Table 1, Figure 1) was approximated by the least squares method using polynomials. For the solid state, the equation was obtained:

\[
H_{298}(t) = 25.815t + 0.02077t^2 - 3.0244 \times 10^{-5}t^3 + 1.630 \times 10^{-8}t^4,
\]

where \( H_{298} \) in J mol\(^{-1}\), \( t = T - 298.15 \), \( T \) in K. The average absolute deviation of points from equation (1) was 38 J/mol. Melt enthalpy depends linearly on temperature:

\[
H_{298}(t_1) = 27453 + 45.38t_1,
\]

where \( t_1 = T - 927.3 \) K. The average absolute deviation of points from equation (2) was 0.075% or 25.4 J mol\(^{-1}\) (figure 2). Table 3 shows the recommended values of the caloric properties of Cs\textsubscript{72.9}Bi\textsubscript{27.1} alloy.

### Table 1. Experimental enthalpy of the Cs\textsubscript{72.9}Bi\textsubscript{27.1} alloy.

| \( T \) (K) | \( H_{298} \) (J mol\(^{-1}\)) | \( T \) (K) | \( H_{298} \) (J mol\(^{-1}\)) |
|------------|-----------------|------------|-----------------|
| 431.7      | 3809            | 828.3      | 16339           |
| 456.5      | 4469            | 877.2      | 17926           |
| 481.2      | 5282            | 916.8      | 19123           |
| 505.9      | 5980            | 951.8      | 28568           |
| 530.7      | 6791            | 976.7      | 29702           |
| 555.4      | 7516            | 1001.6     | 30849           |
| 580.2      | 8352            | 1025.7     | 31907           |
| 629.5      | 9938            | 1051.7     | 33100           |
| 679.0      | 11582           | 1076.3     | 34144           |
| 679.1      | 11558           | 1101.6     | 35379           |
| 729.9      | 13189           | 1126.7     | 36468           |
| 777.9      | 14632           | 1151.8     | 37711           |
| 778.1      | 14591           | 1176.9     | 38768           |
Figure 1. Experimental enthalpy and temperature dependence of heat capacity of Cs\textsubscript{72.9}Bi\textsubscript{27.1} alloy in the solid and liquid states. \textit{AS} – solid phase, \textit{LB} – melt. \textit{1} – experimental enthalpy, \textit{2} – enthalpy approximation, \textit{3} – heat capacity.

Figure 2. Relative deviations of experimental enthalpy of the liquid Cs\textsubscript{72.9}Bi\textsubscript{27.1} alloy from equation (2). \(\delta H_{298} = (H_i / H_{app} - 1) \times 100\%\). \(H_i\) and \(H_{app}\) – measured and smoothed values of melt enthalpy.
The enthalpy change on melting is $\Delta H_f = (7968 \pm 46)$ J mol$^{-1}$. The heat capacity calculated by differentiation of equations (1, 2) is shown in Figure 1. It turns out that in the liquid state the heat capacity of the alloy exceeds the heat capacity of liquid bismuth by 50-57%, and cesium by 41-54%.

Table 2. Recommended values of caloric properties of Cs$_{72.9}$Bi$_{27.1}$ alloy.

| Phase | $T$ (K) | $H_{298}$ (J mol$^{-1}$) | $C_p$ (J mol$^{-1}$ K$^{-1}$) |
|-------|---------|--------------------------|-------------------------------|
| Solid | 298.15  | 0                        | 25.81                         |
|       | 300     | 48                       | 25.89                         |
|       | 350     | 1390                     | 27.73                         |
|       | 400     | 2814                     | 29.17                         |
|       | 450     | 4302                     | 30.26                         |
|       | 500     | 5835                     | 31.04                         |
|       | 550     | 7401                     | 31.56                         |
|       | 600     | 8988                     | 31.88                         |
|       | 650     | 10587                    | 32.04                         |
|       | 700     | 12190                    | 32.09                         |
|       | 750     | 13794                    | 32.08                         |
|       | 800     | 15397                    | 32.05                         |
|       | 850     | 17000                    | 32.07                         |
|       | 900     | 18606                    | 32.17                         |
|       | $T_L$   | 927                      | 19485                         |
|       | $T_L$   | 927                      | 27453                         |
|       |         | 950                      | 28483                         |
|       |         | 1000                     | 30752                         |
| Melt  | 1050    | 33021                    | 45.38                         |
|       | 1100    | 35290                    | 45.38                         |
|       | 1150    | 37559                    | 45.38                         |
|       | 1175    | 38694                    | 45.38                         |

Figure 3 shows the relative deviation of the experimental enthalpy and heat capacity of the Cs$_{72.9}$Bi$_{27.1}$ alloy in the liquid state from their additive values. The data on the caloric properties of bismuth and cesium are taken from [7] and [8], respectively. A significant positive deviation of the caloric properties from the laws for ideal solutions indirectly confirms the assumption that there are complexes in the melt with a partially ionic character of interatomic interaction.

**Conclusion**

Experimental data on the enthalpy and heat capacity of the Cs$_{72.9}$Bi$_{27.1}$ alloy in solid and liquid states were obtained for the first time. It has been established that the heat capacity of the liquid alloy remains constant when overheated over the liquidus. It is shown that the caloric properties of the alloy are significantly different from the calculations according to the laws for ideal solutions.
Figure 3. Relative deviation of the measured values of the caloric properties of the Cs_{72.9}Bi_{27.1} melt from calculations according to the additivity rule. $y = H_{298}$ or $C_p$; \( \delta y = \left( \frac{y_{exp}}{y_{add}} - 1 \right) \times 100\% \).

Acknowledgement
This work was supported by the Russian Science Foundation, grant No. 16-19-10023-II.

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