Calorical properties of equiatomic alloy of rubidium-bismuth system in the temperature range 293–1175 K

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Abstract. The caloric properties of the Rb\textsubscript{50}Bi\textsubscript{50} alloy were experimentally investigated in the temperature range 432.6-1176.8 K with the errors of 1.3% for enthalpy and 0.4% for heat capacity. The enthalpy change on melting was 8844 J mol\textsuperscript{-1}. It is shown that the heat capacity of the melt decreases linearly with overheating above the liquidus and significantly exceeds the heat capacity of the ideal solution. Tables of recommended values of caloric properties over the range from 298.15 K to 1175 K were developed.

1. Introduction
The melts of the rubidium – bismuth system exhibit anomalous properties, which is associated with the formation of ionic bonds between the atoms of the metals [1-2]. This assumption is based on a significant difference in the electronegativity of the components. However, it should be noted that the theory of this phenomenon is insufficiently developed. The range of systems in which a metal-nonmetal concentration transition is observed is not defined, it is not completely clear how it relates to the properties of components and the type of phase diagram. First of all, this is due to the lack of detailed and reliable experimental data on many physicochemical and, in particular, caloric properties of metallic liquid alloys, in which the ionic character of interatomic interaction arises. The aim of this work is to obtain experimental data on the enthalpy and heat capacity of equiatomic alloy of the rubidium-bismuth system over a wide temperature range of solid and liquid states.

2. Experimental details
The caloric properties were studied by the mixing method on isoperibol drop calorimeter [3]. A sample of the alloy Rb\textsubscript{50}Bi\textsubscript{50} was prepared from rubidium and bismuth with a purity of 99.9 wt. % and 99.98 wt. %, respectively. The concentration of the components was determined by the weighting method. The molecular weight of the alloy was 147.200 g mol\textsuperscript{-1}. All operations with the sample, including sealing the ampoule from stainless steel by arc welding, were carried out in a box with a protective atmosphere (Ar, 99.992% by volume).

The temperature of the ampoule was measured by platinum – platinum/rhodium (type S) thermocouple, immersed into the sample in a protective sleeve. The enthalpy of the ampoule was measured in the used calorimeter, which allowed determining the heat loss during a dropping. The fall time (about 0.6 sec) was monitored by an infrared sensor, which was located directly in front of the calorimetric block. The ampoule mass was 39.334 g, and the sample mass was 34.319 g. The ratio of the enthalpy of the sample to the enthalpy of the ampoule varied from 0.33 (457 K) to 0.48 (1177 K). The error of the ampoule enthalpy gives the main contribution to the error of the alloy enthalpy. Another important source of errors in measuring of the alloy properties is a concentration gradient of components.
into the sample. Previous measurements of the mutual diffusion coefficients of the rubidium-bismuth system in the liquid state [4] allowed estimating the time of melt homogenization for Rb50Bi50. It turned out that exposure in the liquid state during 1-1.5 hours is sufficient for the sample homogenization. Therefore, before each dropping of the ampoule, it was kept at a temperature above the melting point during the specified time. A confirmation of the sufficiency of this procedure was the high reproducibility of measurement results, which were carried out alternately at high and low temperatures.

3. Results and Discussion

The phase diagram of the rubidium-bismuth system in the equiatomic composition region has not been studied in sufficient details. It is assumed that an intermetallic compound RbBi does exist, but it has not been reliably confirmed yet (figure 1) [5]. Thermal analysis of the Rb50Bi50 alloy, carried out using a calorimeter furnace and the ampoule with the sample for measuring enthalpy, has shown the presence of a single thermal effect at

\[ T_L = 643.9 \pm 1.5 \text{ K}. \]  

(1)

This, as well as the presence of significant melt undercooling (up to 20 K), indirectly confirms the existence of the RbBi intermetallic compound. The value of the melting point (1) is consistent with the data of [5], where \( T_L = 643 \pm 5 \text{ K} \) and the results of our measurements of the density of this melt \( T_L = 645.5 \pm 1.5 \text{ K} \) [2].

![Phase diagram of Rb-Bi system](image)

**Figure 1.** Phase diagram of Rb-Bi system [5].

Undercooling of the served to obtain data of the liquid alloy at the temperature (629.6 K) below \( T_L \). Note that the transition to the metastable state did not lead to a change in the character of enthalpy temperature dependence.
Due to the lack of data on the heat capacity of Rb50Bi50 in the region of room temperature, the reduction of the measurement results to 293.15 K was carried out according to the iteration procedure described in [6].

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

$$H_{298}(t) = 26.81 \times t + 0.00149 \times t^2,$$

(2)

where $H_{298}$ in J mol$^{-1}$, $t = T - 298.15$, $T$ in K. The average absolute deviation of points from equation (2) was 10 J mol$^{-1}$.

Processing of the primary data according to the procedure [7] has shown that the heat capacity of the liquid alloy linearly decreases with temperature. For this reason, the melt enthalpy Rb50Bi50 was approximated by a second-degree polynomial:

$$H_{298}(t_1) = 18292 + 39.47 \times t_1 - 0.00128 \times t_1^2,$$

(3)

where $t_1 = T - 643.9$ K. The average absolute deviation of experimental points from equations (3) was 0.11% or 30 J mol$^{-1}$ (figure 2). Table 2 shows the recommended values of the caloric properties of Rb50Bi50 alloy. The enthalpy change on melting was $\Delta H_f = (8844 \pm 32)$ J mol$^{-1}$. The heat capacity calculated by differentiation equations (2, 3) is shown in figure 3. It is seen that in the liquid state the heat capacity of the alloy exceeds the heat capacity of liquid bismuth by 26-35%, and rubidium by 16-30%.

![Figure 2. Relative deviations of experimental enthalpy of Rb50Bi50 alloy from equations (2, 3). $\delta H_{298} = (H_i / H_{app} - 1) \times 100\%$. $H_i$ and $H_{app}$ are measured and smoothed values of the enthalpy, respectively.](image)
Table 1. Experimental enthalpy of the Rb50Bi50 alloy.

| $T$ (K) | $H_{298}$ (J mol$^{-1}$) | $T$ (K) | $H_{298}$ (J mol$^{-1}$) |
|--------|----------------------|--------|----------------------|
| 456.6  | 4293                 | 728.3  | 21616                |
| 481.2  | 4952                 | 827.5  | 25518                |
| 506.0  | 5609                 | 877.1  | 27383                |
| 555.3  | 6995                 | 926.7  | 29338                |
| 580.1  | 7677                 | 976.5  | 31324                |
| 604.7  | 8365                 | 1026.6 | 33183                |
| 629.6  | 17686                | 1076.5 | 35163                |
| 654.2  | 18712                | 1126.1 | 36983                |
| 678.8  | 19709                | 1176.8 | 38984                |
| 456.6  | 4293                 |        |                      |

Figure 3. The heat capacity of the Rb50Bi50 alloy and its components in the solid and liquid states.  
1 – Rb50Bi50, 2 – bismuth [7], 3 – rubidium [8]. AS is the solid state, LB is the melt.
Table 2. Recommended values of caloric properties of Rb$_{50}$Bi$_{50}$ alloy.

| Phase | $T$ (K) | $H_{298}$ (J mol$^{-1}$) | $C_p$ (J mol$^{-1}$ K$^{-1}$) |
|-------|---------|--------------------------|-------------------------------|
|       | 298.15  | 0                        | 26.81                         |
|       | 300     | 50                       | 26.82                         |
|       | 350     | 1394                     | 26.96                         |
|       | 400     | 2746                     | 27.11                         |
| Solid | 450     | 4106                     | 27.26                         |
|       | 500     | 5472                     | 27.41                         |
|       | 550     | 6847                     | 27.56                         |
|       | 600     | 8229                     | 27.71                         |
|       | $T_L$   | 643.9                    | 27.84                         |
|       | $T_L$   | 643.9                    | 27.84                         |
|       | 650     | 18533                    | 39.47                         |
|       | 700     | 20503                    | 39.33                         |
|       | 750     | 22466                    | 39.20                         |
|       | 800     | 24423                    | 39.07                         |
|       | 850     | 26373                    | 38.95                         |
| Melt  | 900     | 28317                    | 38.82                         |
|       | 950     | 30255                    | 38.69                         |
|       | 1000    | 32186                    | 38.56                         |
|       | 1050    | 34111                    | 38.43                         |
|       | 1100    | 36029                    | 38.30                         |
|       | 1150    | 37941                    | 38.18                         |
|       | 1175    | 38895                    | 38.11                         |

Conclusions
Experimental data on the enthalpy and heat capacity of the Rb$_{50}$Bi$_{50}$ alloy in solid and liquid states have been obtained for the first time. The measured values of the enthalpy and heat capacity of the alloy in the temperature range $T_L$ – 1175 K exceed additive values by 9–18% and 30–16%, respectively. This discrepancy can be explained by the formation in the melt of ionic bonds and their destruction with increasing the temperature.

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References
[1] Xu R, Kinderman R and van der Lugt W 1991 J. Phys.-Condens. Mat. 3 127
[2] Stankus S V, Abdullaev R N and Khairulin R A 2018 High Temp. High Press. 47 403
[3] Stankus S V, Savchenko I V and Yatsuk O S 2017 Instrum. Exp. Tech. 60 608
[4] Khairulin R A, Stankus S V and Abdullaev R N 2018 J. Eng. Thermophys. 27 303
[5] Pelton A D and Petric A 1993 J. Phase Equilib. 14 368
[6] Stankus S V, Savchenko I V, Yatsuk O S and Raschektaeva E P 2018 Russ. J. Phys. Chem. A 92 1654
[7] Stankus S V, Savchenko I V and Yatsuk O S 2018 High Temp. 56 33
[8] Gurvich L V et al 1982 Thermodynamic Properties of Pure Substances. Handbook vol 4 book 2, ed V P Glushko (Moscow: Nauka) p 464 (in Russian)