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Abstract

Full Text

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Chemistry

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STUDY OF THE THERMODYNAMIC PROPERTIES OF THE TERNARY METALLIC SYSTEM BISMUTH–COPPER–ANTIMONY

(Presented by Academician A. A. Bochvar, 19 XII 1963)

In order to study the effect of the composition of ternary Bi–Cu–Sb solutions with the ratio $N_{\mathrm{Bi}} : N_{\mathrm{Sb}} = 1 : 3$ on their thermodynamic characteristics, we measured the electromotive forces of concentration cells of the type:

$$-\mathrm{Cu}_{(s)} \mid \mathrm{CuCl},\ \mathrm{KCl}-\mathrm{NaCl} \mid [\mathrm{Bi}(N_{\mathrm{Bi}}) - \mathrm{Cu}(N_{\mathrm{Cu}}) - \mathrm{Sb}(N_{\mathrm{Sb}})]^{+}_{(\ell)}.$$

Measurements were carried out for fifteen melt electrodes in the range of copper concentrations N_{Cu} from 0.0516 to 0.8880 at temperatures from 1115 to 1215°K. The absolute error in measuring E did not exceed 0.6 mV.

The metals we used were of the following purity: copper–electrolytically pure, bismuth–analytical-reagent grade, antimony–zone-melted (99.99% Sb). The compositions of the alloys were checked after the experiment by quantitative chemical analysis.

The data obtained make it possible, within the limits of the experimental inaccuracy, to construct straight lines $E = f(t)$, some of which are shown in Fig. 1.

From the data on the value of E at 1215°K, the values $\Delta\overline{Z}^{\mathrm{ex}}_{\mathrm{Cu}}$, $\Delta\overline{H}_{\mathrm{Cu}}$, and $\Delta\overline{S}^{\mathrm{ex}}_{\mathrm{Cu}}$ were calculated (Fig. 2) by the formulas given in ([1–3]). The quantities $\Delta Z^{\mathrm{ex}}_{1:3}$ and $\Delta H_{1:3}$ were calculated by the Darken method ([4]), and the quantity $\Delta S^{\mathrm{ex}}_{1:3}$ from the equation

$$1215\Delta S^{\mathrm{ex}}_{1:3} = \Delta H_{1:3} - \Delta Z^{\mathrm{ex}}_{1:3}.$$

In calculating the quantities $\Delta Z^{\mathrm{ex}}_{1:3}$ and $\Delta H_{1:3}$, we used our experimental values of ΔZ^{ex} and ΔH for the melt BiSb_3, equal to −401 and −837 cal/g-atom, respectively.

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Fig. 1

Figure 1: Fig. 1

Fig. 2. Dependence of $\Delta\overline{Z}^{\text{ex}}_{\text{Cu}}$ (1), $\Delta Z^{\text{ex}}_{1:3}$ (2), $\Delta\overline{H}^{\text{ex}}_{\text{Cu}}$ (3), $\Delta H^{\text{ex}}_{1:3}$ (4), $\Delta\overline{S}^{\text{ex}}_{\text{Cu}}$ (5), and $\Delta S^{\text{ex}}_{1:3}$ (6) on the composition of Bi—Cu—Sb solutions with $N_{\text{Bi}} : N_{\text{Sb}} = 1 : 3$ at 1215°K

Figure 2: Fig. 2. Dependence of $\Delta\overline{Z}^{\text{ex}}_{\text{Cu}}$ (1), $\Delta Z^{\text{ex}}_{1:3}$ (2), $\Delta\overline{H}^{\text{ex}}_{\text{Cu}}$ (3), $\Delta H^{\text{ex}}_{1:3}$ (4), $\Delta\overline{S}^{\text{ex}}_{\text{Cu}}$ (5), and $\Delta S^{\text{ex}}_{1:3}$ (6) on the composition of Bi—Cu—Sb solutions with $N_{\text{Bi}} : N_{\text{Sb}} = 1 : 3$ at 1215°K

Fig. 1. Dependence of emf on temperature for Bi–Cu–Sb melts with $N_{\text{Bi}} : N_{\text{Sb}} = 1 : 3$ of different composition. Atomic fractions of copper: 1 –0.2197; 2 –0.3925; 3 –0.5308; 4 –0.6440; 5 –0.7382.

Figure 2 gives data on the integral excess isobaric mixing potential $\Delta Z^{\text{ex}}_{1:3}$ of Bi–Cu–Sb solutions with $N_{\text{Bi}} : N_{\text{Sb}} = 1 : 3$. They show negative deviations from Raoult' s law. The extremum of the curve is shifted toward pure copper. The minimum value $\Delta Z^{\text{ex}}_{1:3} = -1271$ cal/g-atom corresponds to the composition $N_{\text{Cu}} = 0.65$.

The curve $\Delta H_{1:3}$ (Fig. 2) represents the dependence of the heat of mixing on composition in Bi–Cu–Sb melts with a constant ratio of the concentrations of bismuth and antimony equal to 1 : 3. This curve has an S-shaped form and lies entirely in the negative region. Consequently, the ternary melts under discussion are formed with evolution of heat at any copper content. The maximum and minimum values of the heat of mixing $\Delta H_{1:3}$ are, respectively, −580 cal/g-atom at $N_{\text{Cu}} = 0.22$ and −1100 cal/g-atom at $N_{\text{Cu}} = 0.715$.

The curve $\Delta S^{\text{ex}}_{1:3}$ in Fig. 2 represents the concentration dependence of the excess entropy of mixing in Bi–Cu–Sb solutions with $N_{\text{Bi}} : N_{\text{Sb}} = 1 : 3$.

The course of the curve reveals an interesting regularity. At low copper concentrations the excess entropy of mixing is negative in sign; at a concentration $N_{\text{Cu}} = 0.135$ the integral excess entropy of mixing changes sign to the opposite one. The quantity $\Delta S^{\text{ex}}_{1:3}$ becomes greatest at the composition $N_{\text{Cu}} = 0.45$. At compositions $N_{\text{Cu}} > 0.9$, the entropy of the ternary melt Bi—Cu—Sb with $N_{\text{Bi}} : N_{\text{Sb}} = 1 : 3$ approaches the ideal value.

Fig. 2. Dependence of $\Delta\overline{Z}^{\text{ex}}_{\text{Cu}}$ (1), $\Delta Z^{\text{ex}}_{1:3}$ (2), $\Delta\overline{H}^{\text{ex}}_{\text{Cu}}$ (3), $\Delta H^{\text{ex}}_{1:3}$ (4), $\Delta\overline{S}^{\text{ex}}_{\text{Cu}}$ (5), and $\Delta S^{\text{ex}}_{1:3}$ (6) on the composition of Bi—Cu—Sb solutions with $N_{\text{Bi}} : N_{\text{Sb}} = 1 : 3$ at 1215°K.

Such an unusual course of the $\Delta S^{\text{ex}}_{1:3}$ curve can be explained qualitatively as follows. At small amounts of copper in ternary melts Bi—Cu—Sb with $N_{\text{Bi}} : N_{\text{Sb}} = 1 : 3$, the entropy of mixing is apparently affected by the change in the mixing volume of the components Bi and Sb, whose atomic volumes are approx-

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imately the same. Since at $N_{\mathrm{Cu}} < 0.155$, $\Delta S^{\mathrm{ex}}_{1:3} < 0$, it follows that Bi—Cu—Sb melts with $N_{\mathrm{Bi}} : N_{\mathrm{Sb}} = 1 : 3$ and a low copper content are formed with contraction. As the copper content in these melts increases, the positive contribution to the entropy of mixing, due to the considerable difference between the atomic volumes of bismuth and copper, and of antimony and copper, increases in absolute value. At compositions $N_{\mathrm{Cu}} > 0.155$, the positive contribution to the entropy exceeds the negative contribution from the change in the mixing volume of the ternary melt. The quantity $\Delta S^{\mathrm{ex}}_{1:3}$ thereby becomes greater than zero.

Calculation of the relative errors in determining the integral thermodynamic quantities gives 3.2% for $\Delta Z^{\mathrm{ex}}_{1:3}$, 20% for $\Delta H_{1:3}$, and 38% for $\Delta S^{\mathrm{ex}}_{1:3}$.

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Note: Figure translations are in progress. See original paper for figures.

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