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Abstract

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THERMODYNAMIC PROPERTIES OF Ag–Bi MELTS

As a result of studying the electromotive forces (e.m.f.) of galvanic cells:

$$\mathrm{Ag}\,|\,\mathrm{Ag}^{1+}_{\text{in melt}}\,\mathrm{AgJ}+\mathrm{NaJ}+\mathrm{KJ}\,|\,\mathrm{Ag}\text{—}\mathrm{Bi}_{(\text{melt})}$$

as a function of temperature (650-850° C) and the composition of the alloys, we determined the thermodynamic properties of the Ag–Bi system in the liquid state at 1000° K. The experimental procedure was described earlier ([1]). For preparing the alloys, silver obtained from "pure" grade Ag_2O by thermal decomposition was used, and bismuth from chemically pure Bi_2O_3, reduced with hydrogen. Most of the alloys were analyzed after the experiments, and, as is seen from Table 1, during the course of the experiment the composition of the alloys practically did not change. We observed no signs of electrochemical interaction between the melt and the electrolyte, and the reproducibility of the e.m.f. values was not worse than 0.5%. The experimental data obtained by us are given in Table 1, and the thermodynamic quantities of alloy formation from liquid components, calculated in the usual way, are given in Table 2 and in Figs. 1 and 2.

Table 1

Experimental data for Ag–Bi alloys at 1000° K

X_{Ag} taken	X_{Ag} found	E, mV	dE/dT, mV/100° C	a^*_{Ag}	$\Delta \bar{H}^*_{Ag}$, kcal/g-at	$\Delta \bar{S}^*_{Ag}$, e.u./g-at	Liquidus temperature, °C, our data without taking into account solubility of Bi in Ag	Liquidus temperature, °C, our data taking into account solubility of Bi in Ag	Liquidus temperature, °C, according to ([4,5])
0.097	0.092	135.9	36.5	0.207	5.28	8.42	355	357	293
0.207	–	93.2	28.6	0.339	4.59	6.60	401	405	359
0.323	0.309	66.2	22.8	0.464	3.74	5.26	437	443	388
0.454	–	47.8	18.2	0.574	3.09	4.20	464	473	423
0.564	0.558	35.5	16.0	0.662	2.86	3.69	505	518	450
0.682	0.679	20.3	12.7	0.790	2.47	2.93	567	586	521
0.781	–	6.4	11.2	0.928	2.44	2.58	670	689	669

* Standard state —solid silver.

The phase diagram of the Ag–Bi system is a simple eutectic with very narrow regions of solid solutions ([3]). Over a broad range of compositions, on cooling the alloys practically pure silver precipitates from them, and this permits, in extrapolating data on the dependence

Table 2

Energetics of liquid Ag–Bi alloys at 1000° K*

x_{Ag}	a_{Ag}	a_{Bi}	ΔZ^{ex}, kcal/g-at	ΔH, kcal/g-at	ΔS^{ex}, e.u./g-at	x_{Ag}	a_{Ag}	a_{Bi}	ΔZ^{ex}, kcal/g-at	ΔH, kcal/g-at	ΔS^{ex}, e.u./g-at
0.1	0.164	0.909	+116	+0.30	+0.18	0.5	0.479	0.619	+168	+0.65	+0.47
0.2	0.258	0.844	+186	+0.52	+0.33	0.6	0.535	0.540	+101	+0.55	+0.44
0.3	0.341	0.769	+207	+0.65	+0.43	0.7	0.624	0.402	+15	+0.39	+0.35
0.4	0.417	0.691	+174	+0.69	+0.47	0.8	0.745	0.233	−52	+0.18	+0.22

Fig. 1. Energetics of the Ag—Bi system at 1000° K.

Figure 1: Fig. 1. Energetics of the Ag—Bi system at 1000° K.

x_{Ag}	a_{Ag}	a_{Bi}	ΔZ^{ex}, kcal/g-at	ΔH, kcal/g-at	ΔS^{ex}, e.u./g-at	x_{Ag}	a_{Ag}	a_{Bi}	ΔZ^{ex}, kcal/g-at	ΔH, kcal/g-at	ΔS^{ex}, e.u./g-at
						0.9	0.87	0.11	−20	+0.05	+0.1

* Standard state—liquid components; for recalculation according to (2) the following were taken: melting temperature of silver 1234° K, heat of fusion 2.69 kcal/g-at.

E.m.f. from the temperature to a zero value of the e.m.f. makes it possible to obtain directly the liquidus temperature of the corresponding alloys. As is seen from Table 1, good agreement with the literature data ([4,5]) is found only at high temperatures. If one takes into account that a solid solution of bismuth in silver precipitates, this does not help matters, since in that case (see Table 1) the calculated liquidus temperature is raised still further (the values for the solubility of Bi in solid Ag were taken by us from ([3])). Probably, at lower temperatures there is a change in the entropy of mixing of the alloys, associated with a change in the coordination number, and the dependence of e.m.f. on temperature ceases to be linear. This phenomenon requires further study.

Fig. 1. Energetics of the Ag—Bi system at 1000° K. *a*—our data, obtained in an iodide electrolyte; *b*—data ([6]), obtained in a chloride electrolyte; *c*—data ([7]), obtained in a bromide electrolyte.

There are data in the literature on the study of the e.m.f. of Ag—Bi melts; however, unlike our work, melts of lithium and potassium chlorides ([6]) and of lithium and potassium bromides ([7]) were used as the electrolyte. Data on the energetics of the Ag—Bi system, obtained using all these electrolytes, are given in Fig. 1. Comparing them with ours, one may say that in general they all resemble one another, although attention should be drawn to the fact that the data obtained in experiments with a bromide electrolyte always lie between the data obtained in experiments with chlorides and iodides. In Table 3 we give data on the enthalpies of formation, in kilocalories per 1 g-equiv. at 298° K, of the corresponding silver and bismuth salts ([2]), and the values of the electrode potentials of these metals (in volts) in the corresponding salts relative to sodium, according to Delimarskii ([8]).

From Table 3 it is evident that, when bromides and chlorides are used as the electrolyte, a distorting influence of the electrochemical interaction between the alloy and the electrolyte is possible; this is unlikely when iodides are used (a large difference between the enthalpies of formation and between the electrode potentials), and therefore we are inclined to regard our data on the thermodynamic properties of Ag–Bi melts as more reliable.

We have previously noted (9) the existence of a great similarity in the energetics of the Cu–Sb and Ag–Sb systems; in the case of Cu–Bi and Ag–Bi there is no such similarity. Moreover, in contrast to Cu–Bi alloys, where there are large positive deviations from Raoult' s law (10), in the Ag–Bi system the positive deviations from Raoult' s law for silver at low contents of it in the alloys are replaced by negative ones when the silver content exceeds 45 at.% (see Fig. 2). Let us also note that if in the series Cu–Sb, Ag–Sb and Au–Sb the complexity of the phase diagrams decreases (see (3)), then in the series Cu–Bi, Ag–Bi and Au–Bi the opposite relationship is observed. It is probable that in all these alloys the interaction of the electronic shells of the atoms plays a very large role, and their behavior can be understood only after this interaction has been studied.

Fig. 2. Activities of the components in the Ag–Bi system at 1000° K

Table 3

Enthalpies of formation (upper number) (2) and electrode potentials (8) of the corresponding Bi and Ag salts

Cation	Cl^{1-}	Br^{1-}	J^{1-}
Ag^{1+}	30.5 ± 0.1+2.33	23.70 ± 0.1+2.11	15.34 ± 0.1+1.75
Bi^{3+}	30.2 ± 0.7+2.23	19.3 + 2.7+2.15	8.0 + 1.75+2.08

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named after M. V. Lomonosov

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