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Abstract

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THERMODYNAMIC PROPERTIES OF Ag–Sb MELTS

To determine the thermodynamic properties of Ag–Sb melts, we studied the dependence of the electromotive force (e.m.f.) on the temperature and composition of the alloys for the following galvanic cell:

$$\mathrm{Ag}_{(\mathrm{solid})} \,|\, \mathrm{Ag}^{+}_{(\mathrm{in\ melt\ KJ+NaJ+AgJ})} \,|\, \mathrm{Ag—Sb}_{(\mathrm{melt})}$$

The experiments were carried out in a nitrogen atmosphere at temperatures of 630–830° C. In all, 8 alloys were investigated, the composition of which lay within the range 10.3–79.5 at. % silver. The procedure for carrying out the experiments and the course of the calculations were

Table 1

Experimental data for liquid alloys of silver with antimony at 1000° K

x_{Ag}	E, mV	dE/dT, mV/100°	a^{*}_{Ag}	$\overline{\Delta H}^{*}_{\mathrm{Ag}}$, kcal/g-at	$\overline{\Delta S}^{*}_{\mathrm{Ag}}$, e.u./g-at	a^{**}_{Ag}	$\overline{\Delta H}^{**}_{\mathrm{Ag}}$, kcal/g-at	$\overline{\Delta S}^{**}_{\mathrm{Ag}}$, e.u./g-at
0.103	202.4	41.1	0.095	4.66	9.48	0.074	1.97	7.30
0.203	161.0	31.5	0.154	3.55	7.26	0.119	0.86	5.08
0.295	139.0	26.0	0.199	2.79	6.00	0.154	0.10	3.82
0.395	120.4	21.7	0.247	2.24	5.00	0.192	−0.45	2.82
0.498	103.7	17.6	0.300	1.66	4.06	0.232	−1.03	1.88
0.613	86.8	13.8	0.365	1.18	3.18	0.283	−1.51	1.00
0.694	61.8	10.2	0.488	0.92	2.36	0.378	−1.77	0.18
0.795	23.2	10.0	0.764	1.78	2.31	0.591	−0.91	0.13

* Standard states–solid silver and liquid antimony.
** Standard states–liquid components; for conversion to liquid silver, the heat of fusion of silver was taken according to ([4]) as 2.69 kcal/g-atom, m.p. 1234° K.

described earlier ([1]). The experimental data are given in Table 1.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

A complete thermodynamic description of the Ag–Sb system in the liquid state (determination of the isobaric potential, enthalpy, and entropy of formation of the alloys) has been made for the first time. The use as electrolyte of a melt of sodium and potassium iodides, to which a small amount of silver iodide had been added, made it possible to avoid the electrochemical interaction that occurs when a melt of chlorides ([2]) is used as the electrolyte. As a result, the reproducibility of the e.m.f. for each alloy in our experiments was within 0.5%.

The energetics of formation of Ag–Sb alloys at 1000° K are presented by us in Figs. 1 and 2. In general, the system is characterized by negative deviations from Raoult' s law (see Fig. 1) and by negative ΔZ^{isob}, positive ΔS^{isob}, and a complex course of the enthalpies of formation (Fig. 2). This agrees with the phase diagram, which in the region adjacent to silver is rather complex ([3]). In the same figures, for comparison, the corresponding quantities are also given for Cu–Sb melts, determined by us earlier ([5]).

Attention is drawn to the very great similarity in the character of the corresponding curves: minima on the curves ΔZ^{isob} and ΔH and a maximum on the cur-

of ΔS^{excess} in both systems occur for alloys with approximately the same antimony content. The character of the deviation of the component activities from Raoult' s law is also very similar in these systems.

In the phase diagrams of both systems a rather great similarity is also found: the intermetallic phases are grouped on the copper or silver side, and the phases Ag_3Sb and Cu_3Sb exist. However, there are also substantial differences: first, the number of phases in the Cu–Sb system is considerably larger, which indicates a greater intensity of interaction between the components in this system and is also reflected in the thermodynamic properties (see Fig. 2); second, intermetallic compounds in the Cu–Sb system begin to appear at a higher antimony content: there is a compound Cu_2Sb, for which there is no analogue in the Ag –Sb system.

Fig. 1. Activities of the components in the Ag–Sb and Cu–Sb systems at 1000° K. 1, 3 –Ag–Sb system: 1 –a_{Sb}, 3 –a_{Ag}; 2, 4 –Cu–Sb system: 2 –a_{Sb}, 4 –a_{Cu}.

Fig. 2. Comparison of the thermodynamic properties of the Ag–Sb and Cu–Sb systems at 1000° K. 1 –Ag–Sb system, 2 –Cu–Sb system.

Fig. 3. Comparison of the experimental and calculated liquidus curves of the Ag–Sb system

Figure 3: Fig. 3. Comparison of the experimental and calculated liquidus curves of the Ag–Sb system

In connection with this, it is of interest to consider the character of the change in the activity of antimony as a function of composition (Fig. 1). In both systems the positive deviations from Raoult' s law, as the antimony content decreases, pass into negative ones; moreover, in Cu–Sb alloys this transition occurs earlier. This effect is associated with the formation in the melt not only of groupings of the type A–B, but also A_2–B and even A_3–B. It is probable that in Ag –Sb melts the tendency toward the formation of A_3–B groupings is expressed more strongly, in comparison with A_2–B or A–B, than in Cu–Sb melts, where, apparently, A_2–B and A–B groupings are represented relatively more than A_3 –B. This is indirectly indicated by the phase diagram: in the Ag–Sb system there is no compound analogous to Cu_2Sb, or even one with a smaller silver content than the Ag_3Sb phase. It is possible that the complex dependence of the enthalpy of formation of Ag–Sb melts on composition is also connected with this same effect.

Using the well-known thermodynamic proposition concerning the equality of the activities of a component in phases that are in equilibrium, one can calculate the phase diagram of the given system. We carried out such a calculation

for the Ag–Sb system in order to determine the liquidus curve on the antimony side up to the eutectic. This calculation is analogous to one we carried out earlier for the Cu–Sb system[6], and its results are given in Fig. 3. The calculated liquidus curve and the experimentally determined one[7,8] agree well, but the calculated curve lies somewhat higher (by about 10°). This is probably connected with the nonlinear dependence of $\lg a_{Sb}$ on $1/T$, a phenomenon that Kleppa[9] observed in the Au–Sn system. It is possible that, on approaching the liquidus curve, the nature of the packing of atoms in the liquid alloy changes, which should affect the entropy of mixing and, consequently, the temperature coefficient dE/dT. Under the experimental conditions (high melting temperature of the electrolyte), we could not study the activity of the components sufficiently close to the liquidus curve.

Fig. 3. Comparison of the experimental[8,9] (1) and calculated (2) liquidus curves of the Ag–Sb system

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