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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Thermodynamic Properties of Lead–Sodium–Antimony Liquid Alloys

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Abstract—The thermodynamic properties of lead–sodium–antimony liquid alloys were determined by the emf method. The thermodynamic properties of the edge binary systems, sodium–lead, sodium–antimony, and lead–antimony, were analyzed. The possibility of approximately estimating the thermodynamic properties of the ternary system on the basis of data on the edge binary systems using the simplest geometric models was demonstrated. The sodium-containing alloys show significant negative deviations from the ideal behavior. All the data are given for 900 K.

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The interest in studying and using liquid metal current sources with molten electrolytes revived recently. Kim et al. [1] substantiated in detail the appropriateness of developing such energy conversion systems. Alkali metals, magnesium, and alkaline earth metals are considered as negative electrodes, and lead, tin, antimony, bismuth, tellurium, and their alloys can serve as positive electrodes. Wang et al. [2] described a liquid metal current source based on the Li–(Pb–Sb alloy) system and operating at 450°C, with the molten LiF–LiCl–LiI system as electrolyte.

Therefore, it seems appropriate to consider briefly the presently available data on thermodynamic properties of Na–Pb, Na–Sb, and Pb–Sb liquid binary alloys and the results of an experimental study of the Pb–Na–Sb ternary system. As the objectives of this paper are related to technology, we restricted the consideration of the binary and ternary systems to alloys containing up to 50 mol % sodium. In view of relatively high melting point of antimony (903.6 K), the calculations were performed for 900 K.

Sodium–lead system. Three congruently melting compounds, $Na_{15}Pb_4$ (Na_4Pb?), Na_9Pb_4, and NaPb, are formed in the Na–Pb system. They are characterized by relatively flat maxima in the liquidus curve and low melting points: 659, 676, and 645 K, respectively. In the lead-rich part of the system, there is a variable-composition phase of berthollide type with the composition in the interval $0.26 \le x_{Na} \le 0.33$. The thermodynamic properties of Na–Pb liquid alloys were studied in numerous works, mainly by the emf method using solid electrolytes with sodium conductivity (glasses containing Na_2O; sodium polyaluminates: β-alumina or β''-alumina). The nature of the solid electrolytes and the experimental procedure are considered in detail in [3], with a summary of the thermodynamic and other properties of Na–Pb liquid alloys also presented. The thermodynamic properties of sodium–lead liquid alloys were considered in detail for the first time in [4]. All the subsequent studies, differing in the methods used, gave reasonably consistent results. The Na–Pb system exhibits significant negative deviations from the ideal behavior. Theoretical analysis of the concentration dependence of the thermodynamic functions of Na–Pb liquid alloys is performed in [5].

The emf values of circuits, measured at close temperatures, are compared in Table 1. The thermodynamic properties of Na–Pb liquid alloys were also studied by Saboungi et al. [8], but the results were presented only graphically.

Table 1. Values of emf for the Na │ Na^+ │ Na, Pb curcuit, according to results of different studies

x_{Na}	emf of circuit, E, V			
	698 K [4]	698 K [3]	673 K [6]	683 K [7]
0.10	0.476	0.471	0.465	0.465
0.20	0.407	0.403	0.396	0.394
0.30	0.337	0.342	0.328	0.331
0.40	0.266	0.268	0.266	0.266
0.50	0.197	0.197	0.198	0.197

Table 2. Enthalpy of mixing of sodium–lead liquid alloys, according to data of different authors

x_{Na}	ΔH, kJ mol^{-1}, according to indicated source		
	[3]	[6]	[9]
0.20	–8.53	–7.98	–7.72
0.40	–15.44	–15.06	–14.21
0.60	–18.20	–17.63	–17.18
0.80	–13.85	–13.99	–13.64

The good agreement not only of the emf values obtained for the Na–Pb system but also of the temperature coefficient of emf follows from close values of the enthalpy of mixing, obtained in comparable temperature intervals (Table 2). According to the results of the theoretical analysis, the minimal value of the enthalpy of mixing in the temperature interval under consideration is –18.02 kJ mol^{-1} at $x_{\text{Na}} = 0.6$ [5].

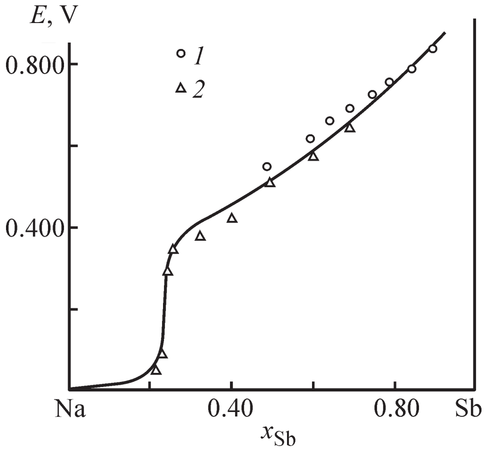

Fig. 1. emf E as a function of the composition of sodium–antimony liquid alloys. Data for 1073 K. Data of (*1*) [12] and (*2*) [13].

The main thermodynamic characteristics of the Na–Pb liquid alloys at 900 K are given in Table 3.

Sodium–antimony system. Two congruently melting compounds, Na_3Sb (mp 1130 K) and NaSb (mp 738 K), are formed in the Na–Sb system [10, 11]. The thermodynamic properties of sodium–antimony liquid alloys were studied for the first time in [12] by the emf method using high-melting Pyrex glass as solid electrolyte in the temperature interval 823–923 K ($0.10 \le x_{\text{Na}} \le 0.50$, 8 compositions). Sangster and Pelton [10] in a review dealing with the Na–Sb system present the results of [12] completely and note with the reference to unpublished Saboungi's work (Argonne National Laboratory, the United States) that the study of this system by the emf method using β-silica as solid electrolyte gave consistent results. Egan [13], also using the emf method with CaF_2 as a fluoride-conducting solid electrolyte, studied the thermodynamic properties of Na–Sb liquid alloys ($0.300 \le x_{\text{Na}} \le 0.788$, 9 compositions) at 1073 K. The emf values obtained by Egan [13] and our data extrapolated to this temperature are compared in Fig. 1. Taking into account relatively high

Table 3. Thermodynamic properties of sodium–lead liquid alloys at 900 K, according to [3]

x_{Na}	E, V	a_{Na}	γ_{Na}	ΔG	ΔG^{exc}
				kJ mol^{-1}	
0.10	0.474	2.21×10^{-3}	2.21×10^{-2}	–5.43	–3.00
0.20	0.405	5.39×10^{-3}	2.70×10^{-2}	–9.44	–5.70
0.30	0.333	1.37×10^{-2}	4.57×10^{-2}	–12.6	–8.04
0.40	0.261	3.46×10^{-2}	8.63×10^{-2}	–14.8	–9.77
0.50	0.189	8.74×10^{-2}	0.175	–15.9	–10.7

temperature of the experiment and significant differences in the experimental procedure (sodium cationic and fluoride anionic conductivity of the electrolyte), the agreement between the data of [12] and [13] is quite satisfactory. The use of anion-conducting solid electrolytes in studying the thermodynamic properties of liquid alloys is considered in detail in [3]. The main thermodynamic characteristics of Na–Sb liquid alloys at 900 K are given in Table 4.

The phase diagram and thermodynamic properties of Na–Sb alloys are described in a recent paper [11], including the relevant data published previously starting from 1906. All the calculation results are compared to the data of [12] and are fully consistent with them at 900 K (Fig. 2).

Lead–antimony system. The Pb–Sb system is a eutectic system (T_{eut} = 525 K, x_{Pb} = 0.175). The thermodynamic properties of Pb–Sb liquid alloys were repeatedly studied by the emf method with molten and solid electrolytes [14]. Among recent studies on thermodynamic properties of Pb–Sb liquid alloys, we can mention papers by Arkhipov et al. [15, 16]. The optimized values of ΔG^{exc} for the Pb–Sb system at 900 K were used in the calculations.

Lead–sodium–antimony system. The Pb–Na–Sb system was studied in the temperature interval 773–873 K in the sections with constant $x_{Pb} : x_{Sb}$ ratios of 3 : 1, 1 : 1, and 1 : 3 in the composition interval $0.1 \le x_{Na} \le 0.5$. The emf method with Pyrex glass as solid electrolyte was used. The experimental procedure is described in [3, 12]. The results obtained were extrapolated to 900 K (Table 5).

The integral molar excess Gibbs energy ΔG^{exc} of the Pb (1)–Na (2)–Sb (3) system was determined along

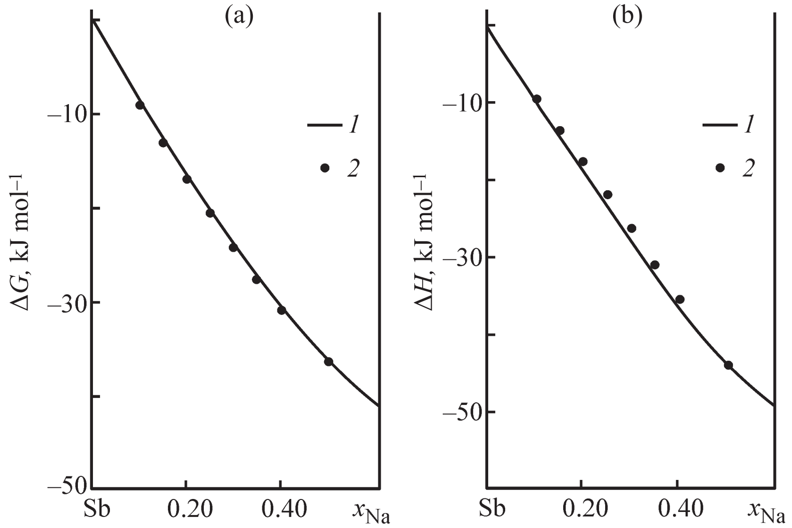

Fig. 2. (a) Integral molar Gibbs energy and (b) enthalpy of mixing ΔH as functions of the composition of sodium–antimony liquid alloys. Data for 900 K. (*1*) Calculation using model [11] and (*2*) experimental data [12].

Table 4. Thermodynamic properties of sodium–antimony liquid alloys at 900 K, according to [3]

x_{Na}	E, V	a_{Na}	γ_{Na}	ΔG	ΔG^{exc}
				kJ mol^{-1}	
0.10	0.860	1.53×10^{-5}	1.53×10^{-4}	–9.10	–6.70
0.20	0.782	4.17×10^{-5}	2.09×10^{-4}	–17.1	–13.3
0.30	0.732	7.94×10^{-5}	2.65×10^{-4}	–24.4	–19.8
0.40	0.667	1.83×10^{-4}	4.58×10^{-4}	–30.9	–25.9
0.50	0.595	4.65×10^{-4}	9.30×10^{-4}	–36.5	–31.3

sections of the concentration triangle with constant $x_1 : x_3$ ratios using the equation

$$\Delta G^{exc} = (1 - x_2)\Big[\int_0^{x_2} \Delta G_2^{exc}/(1 - x_2)^2 \mathrm{d}x_2 + \Delta G^{exc}_{x_2=0}\Big]_{x_1:x_3}. \quad (1)$$

The quantity $\Delta G^{exc}_{x_2=0}$ in Eq. (1) is ΔG^{exc} of the Pb–Sb binary system. The quantities ΔG^{exc} for the calculations were described using the Redlich–Kister polynomial [14] of the following form:

$$Q = \Delta G^{exc}/RT = x_{Sb}(1 - x_{Sb})\,[b + c(2x_{Sb} - 1) + d(2x_{Sb} - 1)^2]. \quad (2)$$

The following coefficients of Eq. (2) were obtained for 900 K: $b = -0.24962$, $c = 0.001013$, $d = -0.00084$, correlation coefficient 0.9999. Calculations with Eq. (1) require knowledge of ΔG^{exc} of the Pb–Sb system at the lead mole fractions of 0.75, 0.50, and 0.25. The values of the Q-function and ΔG^{exc} at these compositions are given in Table 6.

The values of ΔG^{exc} for the Pb–Na–Sb ternary system at 900 K, calculated using Eq. (1), are included in Table 5. The ΔG^{exc} isolines calculated from these data are plotted in Fig. 3.

Starting from the second half of the XX century, geometric models found wide use for calculating the thermodynamic properties of ternary and more complex liquid metal systems on the basis of data on the edge binary systems [17–20]. These models become more and more complicated [21]. The appearance of the calculation models is associated with the fact that the experimental determination of the thermodynamic properties of three-, four-, and five-component metal systems is extremely labor-consuming, and not always a sufficiently reliable investigation method can be chosen. All the models are based on the assumption that pair interactions make a prevalent contribution to an integral thermodynamic property of a ternary or more complex liquid metal system. Pair interactions lead to the formation of associates, clusters, and groups, causing deviations of binary systems from the ideal

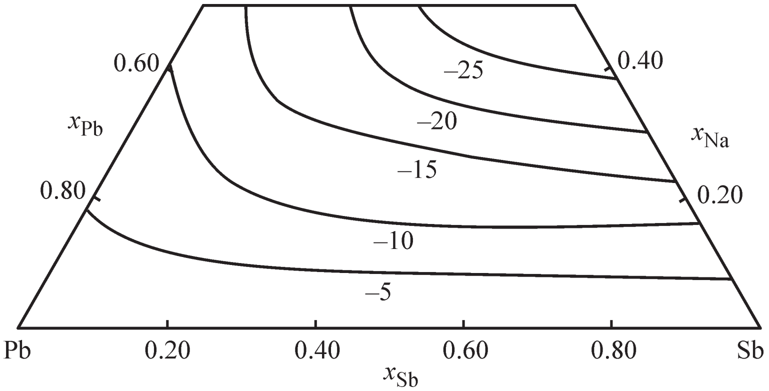

Fig. 3. Isolines of the integral molar excess Gibbs energy (kJ mol^{-1}) of lead–sodium–antimony liquid alloys. Data for 900 K.

Table 5. Thermodynamic properties of lead–sodium–antimony liquid alloys at 900 K

$x_{Pb} : x_{Sb}$	x_{Na}	E, V	ΔG_{Na}, kJ mol^{-1}	a_{Na}	γ_{Na}	ΔG^{exc}_{Na}	ΔG^{exc}
						kJ mol^{-1}	
3 : 1	0.10	0.627	–60.51	3.07×10^{-4}	3.07×10^{-3}	–43.28	–4.91
	0.20	0.545	–52.59	8.86×10^{-4}	4.43×10^{-3}	–40.55	–9.00
	0.30	0.489	–47.19	1.82×10^{-3}	6.07×10^{-3}	–38.20	–13.67
	0.40	0.425	–41.01	4.17×10^{-3}	1.04×10^{-3}	–34.15	–15.75
	0.50	0.320	–30.88	1.61×10^{-2}	3.22×10^{-2}	–25.71	–17.50
1 : 1	0.10	0.708	–68.32	7.40×10^{-5}	7.40×10^{-4}	–53.94	–6.09
	0.20	0.631	–60.89	$2.92\cdot \times 10^{-4}$	1.46×10^{-3}	–48.86	–11.09
	0.30	0.578	–55.78	5.79×10^{-4}	1.93×10^{-3}	–46.77	–15.59
	0.40	0.518	–49.99	1.25×10^{-3}	3.13×10^{-3}	–43.15	–19.76
	0.50	0.452	–43.62	2.94×10^{-3}	5.88×10^{-3}	–38.43	–23.30
1 : 3	0.10	0.788	–76.04	3.86×10^{-5}	3.86×10^{-4}	–58.81	–6.22
	0.20	0.724	–69.87	8.80×10^{-5}	4.40×10^{-4}	–57.83	–12.33
	0.30	0.666	–64.27	1.86×10^{-4}	6.20×10^{-4}	–55.26	–17.96
	0.40	0.594	–57.32	4.71×10^{-4}	1.18×10^{-3}	–50.46	–24.48
	0.50	0.518	–49.99	1.25×10^{-3}	2.51×10^{-3}	–44.80	–28.38

Table 6. Values of the Q-function and ΔG^{exc} at 900 K for lead–antimony liquid alloys

Composition		Q	ΔG^{exc}, kJ mol^{-1}
x_{Pb}	x_{Sb}		
0.75	0.25	–0.04694	–0.351
0.50	0.50	–0.06241	–0.467
0.25	0.75	–0.04368	–0.327

behavior. However, interaction of different kinds of associates with each other is not taken into account in the geometric models. In cases when in two edge systems the component interaction is intense and the third system is close to ideal or regular, relatively simple Bonnier, Toop, and Hillert geometric models are used [17]. The calculation equations have the form

$$\Delta G^{exc} = \left[\frac{x_1}{1-x_2}\Delta G^{exc}_{12} + \frac{x_3}{1-x_2}\Delta G^{exc}_{23}\right]_{x_2} + (1-x_2)[\Delta G^{exc}_{13}]_{x_1/x_3}, \tag{3}$$

$$\Delta G^{exc} = \left[\frac{x_1}{1-x_2}\Delta G^{exc}_{12} + \frac{x_3}{1-x_2}\Delta G^{exc}_{23}\right]_{x_2} + (1-x_2)^2[\Delta G^{exc}_{13}]_{x_1/x_3}, \tag{4}$$

$$\Delta G^{exc} = \left[\frac{x_1}{1-x_2}\Delta G^{exc}_{12} + \frac{x_3}{1-x_2}\Delta G^{exc}_{23}\right]_{x_2} + \frac{4x_1x_3}{(2x_1+x_2)(2x_3+x_2)}[\Delta G^{exc}_{13}]_{x_3+\frac{x_2}{2}}. \tag{5}$$

Table 7. Results of calculating the molar excess Gibbs energy of the lead–sodium–antimony ternary system at 900 K using geometric models

Alloy composition			Calculation of ΔG^{exc} using indicated equation		
x_{Pb}	x_{Na}	x_{Sb}	(3)	(4)	(5)
0.675	0.10	0.225	–4.24	–4.21	–4.21
0.600	0.20	0.200	–7.88	–7.83	–7.82
0.525	0.30	0.175	–11.23	–11.15	–11.15
0.450	0.40	0.150	–14.01	–13.93	–13.92
0.375	0.50	0.125	–16.03	–15.92	–15.94
0.450	0.10	0.450	–5.27	–5.22	–5.23
0.400	0.20	0.400	–9.87	–9.80	–9.80
0.350	0.30	0.350	–14.25	–14.15	–14.16
0.300	0.40	0.300	–18.12	–18.01	–18.01
0.250	0.50	0.250	–21.23	–21.12	–21.18
0.225	0.10	0.675	–6.07	–6.04	–6.04
0.200	0.20	0.600	–11.66	–11.61	–11.61
0.175	0.30	0.525	–17.09	–17.02	–17.02
0.150	0.40	0.450	–22.06	–21.98	–21.18
0.125	0.50	0.375	–28.31	–28.23	–28.23

The corresponding graphic plots are shown in Fig. 4. For Eqs. (3) and (4), the plots are similar (Fig. 4a), and for Eq. (5), the plot is shown in Fig. 4b. As can be seen, Eqs. (3)–(5) differ only in the second term in the right-hand side, which takes into the contribution of the binary system 1–3 to ΔG^{exc} of the ternary system. Because ΔG_{13}^{exc} of the Pb–Sb binary system is very small, the results of the calculations using Eqs. (3)–(5) are very similar (Table 7). The mean deviations of the calculated ΔG^{exc} from the values calculated from the experimental data using Eq. (1) are 12.6% for the section $x_{Pb} : x_{Sb} = 3 : 1$, 10.1% for the section 1 : 1, and 7.6% for the section 1 : 3. All the deviations are of the same sign and show that the real interaction of the components of the ternary system is more intense than it follows from additive summation of the quantities ΔG^{exc} for the edge binary systems. The phase diagram of the Pb–Na–Sb system is unknown. However, a recent study of the phase diagram of the Sn–Na–Sb system, which is structurally similar to the Pb–Na–Sb system, revealed the formation of complex compounds involving all the three components [22]. The presence of such compounds in the solid phase is a prerequisite for the formation of ternary associates in the liquid phase.

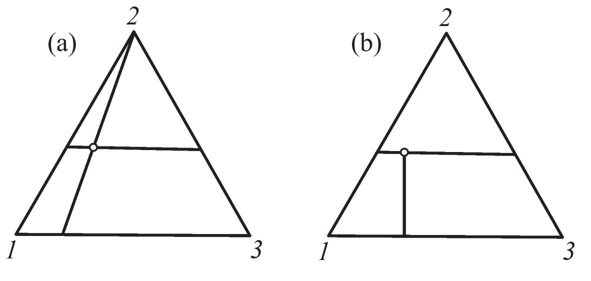

Fig. 4. Geometric interpretation of models for calculating G^{exc} using Eqs. (a) (3) and (4), (b) (5).

CONCLUSIONS

(1) The values of the thermodynamic functions for the edge binary systems Na–Pb and Na–Sb ($x_{Na} \leq 0.50$) at 900 K were recommended on the basis of analysis of the published data.

(2) The thermodynamic properties of Pb–Na–Sb liquid alloys were studied by the emf method. Comparison of the experimentally determined integral molar excess Gibbs energy of the ternary system with the results of the calculation using the geometric models taking into account only pair interactions in the edge binary systems suggests that the associates formed in the Na–Pb and Na–Sb systems interact with each other, increasing the negative deviations of the liquid alloys from the ideal behavior.

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