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Thermodynamic Functions of Mixing the Melts in the Ga–Pb System

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Abstract—On the basis of the data of high-temperature differential mass spectrometry we calculated thermodynamic activities a_i of components in melts of Ga–Pb system. The functions $a_i(x)$ are described in the polynomial representation of excess potentials. The constants of the temperature dependence of the interaction parameters were determined and used for the calculation of the heat of mixing and excess entropy. The spinodal curve of the liquid phase Ga–Pb was built, the stratification critical point temperature (870.7 K) was determined, in agreement with literature data.

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Investigation of properties of condensed phases, including metallic solutions–melts at high temperatures, meets well-known experimental difficulties due to the requirement of the high-temperature equipment. In this respect thermographic, calorimetric, and tenzimetric methods are sufficiently developed. However, direct calorimetric measurement of small thermal effects, like heats of mixing, is a formidable task. There has been developed and remains quite effective an indirect way of obtaining data on the functions of mixing at high temperatures using the results of tensiometry. In a case of a solution, the study of the vapor composition and the measurement of the partial pressures of the components of the condensed phase allow the direct determination of the excess chemical potentials $\Delta\mu_i^E$ of the components. Further problem can be reduced to the choice of a suitable representation (model) of excess potential and, if successful, to the calculation of the partial and integral molar thermodynamic functions. The key role belongs to the investigation of dependence of $\Delta\mu_i^E$ on the composition in the region of homogeneity. The latter, in fact, governs the choice of the model. The dependencies on intensive variables makes it possible to calculate the partial molar excess properties in characteristic form. Of course, the study of the condensed phase–vapor equilibrium cannot be complied with the requirement of constancy of the integral vapor pressure, so the data correspond not to the isobaric-isothermal region of homogeneity, but to the diversity of coexisting states (or its part) of the condensed phase. However, if the integral pressure changes in a fairly limited range, its influence on the thermodynamic properties of the condensed phase can be neglected in many cases.

Another known problem consists in the fact that from the tensiometric data only the partial function of one (or a few) components can be reliably derived. Only in the two-component systems this is sufficient to calculate the properties of the phases, since the potential of the other component is calculated by integrating the isobaric-isothermal Gibbs–Duhem equation. Therefore an analytical representation of the $\Delta\mu_i^E(x)$ function is very desirable. There are many forms of empirical and semiempirical calculation of excess potential, which have their own areas of application [1, 2], but the polynomial representation [3] used in this paper is very convenient.

The phases allowing such a phenomenological description include metal solutions–melts with a complex nature of the interaction, in particular, the liquid phase of the Ga–Pb system characterized by the stratification of monotectic type (Fig. 1). Authors of various publications have no consensus in the estimates of the coordinates of the critical point of stratification. The closest position of researchers concerns determining the critical point temperature (T_k). Thus, Vol and Kagan [4] indicate T_k = 882 K. In [5, 6] the values of 879 K and 879.8 K are given, respectively. More significant are the differences in the determination of the critical point composition. Son et al. [6] believe that the binodal curve is almost symmetrical, and therefore corresponds to the critical point of ~0.50 mole fraction of Ga. Other publications contain the view that the dome has an asymmetric shape, and the critical point is shifted toward the composition of a larger content of gallium and is located at the composition of ~0.60 mole fraction of Ga [4, 5, 7].

The study of the liquid phase of the Ga–Pb system is relevant due to application of these melts in the synthesis of lead telluride films doped with 13 group elements [8]. In previous work [9] we reported on measuring the partial vapor pressure of the components above the liquid phase of the Ga–Pb system. The measurements showed positive deviations from ideality, but the obtained activities of components have not been processed by the Gibbs–Duhem equation, and therefore the data may be inconsistent. This led us to the consideration of the experimental data in order to make calculations based on the polynomial representation of excess potentials, to find the molar mixing function, and to evaluate the critical stratification temperature.

A feature of the A^{III}–Pb systems, where A^{III} is an element of 13-th group of the Mendeleev Periodic Table, is very low volatility of the first component while volatility of lead is significantly higher. At 1000 K the vapor pressure above the melt of pure gallium is 3.21×10^{-4} Pa, while the vapor pressure of atomic lead over the lead melt is 1.51 Pa [10, 11]. Because of such low vapor pressures of gallium, in [9] the partial pressure of lead was measured by high-temperature differential mass spectrometry according to Eq. (1), while the gallium vapor pressure was calculated by the method of comparison of ion currents according to Eq. (2).

$$p_{Pb} = p^0_{Pb}(I_{Pb}/I^0_{Pb}), \qquad (1)$$

$$p_{Ga} = p_{Pb}\,\frac{I_{Ga^+}\sigma_{Pb}\gamma_{Pb}\alpha_{Pb}}{I_{Pb^+}\sigma_{Ga}\gamma_{Ga}\alpha_{Ga}}. \qquad (2)$$

Here p, I, p^0, I^0 are the partial pressure of lead and the intensity of the Pb^+ ion current above the melt of known composition and the melt of pure component, respectively, σ is the cross section of atoms ionization, γ is average effective conversion rate on the first electrode of the secondary electron multiplier of the mass spectrometer proportional to the $M_i^{-1/2}$ (M_i is molar mass), α_i is a correction for isotopic composition.

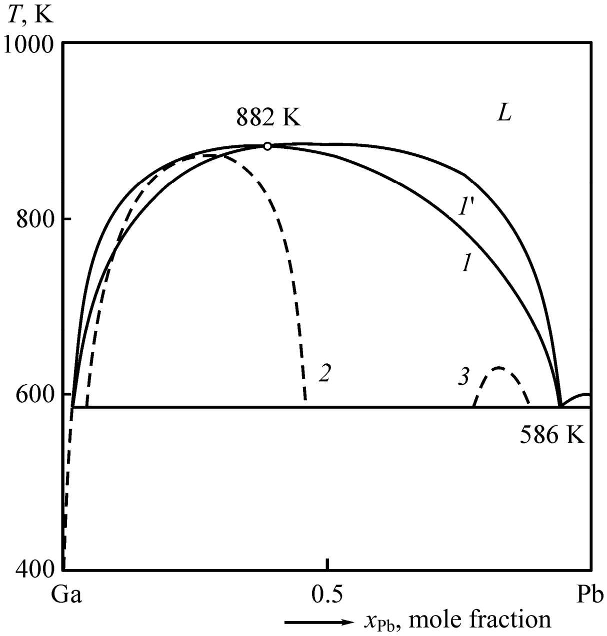

Fig. 1. T, x-State diagram of Ga–Pb system. (*1*) binodal curve according to [4]; (*1'*) binodal curve according to [5]; (*2*, *3*) calculated branches of spinodal curve.

As reported in [9], the mass spectra of vapor over melts of pure metals for the temperature range 780–1050 K contained primarily the ion peaks of Pb^+ and Ga^+. The presence of molecular ions Pb_2^+ corresponded to the peaks of very low intensity, and the ion currents corresponding to dimers Ga_2^+ were at the limit of detectability. Also, the experimental evidence was not obtained for the existence in the vapor of the molecules containing in their structure both gallium and lead.

Activities of the melt components were determined by Eq. (3), the values of p_i^0 were calculated using the reference values [10, 11].

$$a_i = p_i/p_i^0. \qquad (3)$$

However, the obtained values of activity did not satisfy the Gibbs–Duhem equation. The experimental data for lead seem to be too low and not corresponding to the proximity of the stratification critical point, which is firmly established for the Ga–Pb liquid phase at ~880 K. Therefore, as the correct data for further

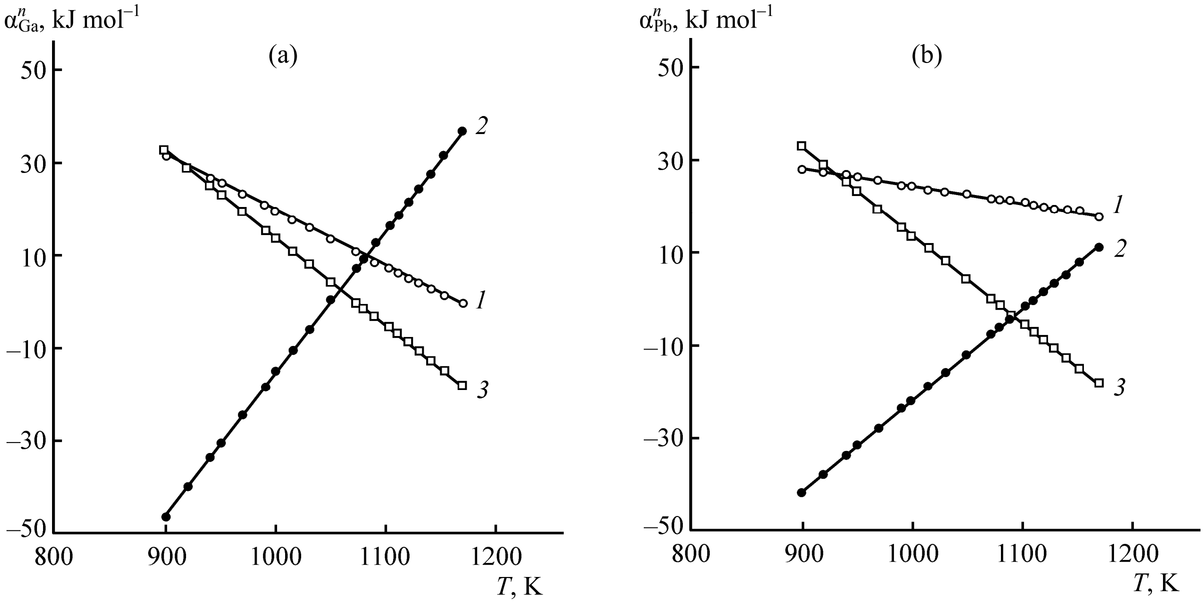

Fig. 2. Dependences of interaction parameters of (a) Ga and (b) Pb on temperature in the melt of Ga–Pb system. (*1*) α^0_i; (*2*) α^1_i; and (*3*) α^2_i.

calculations of the thermodynamic functions the values of the partial pressure of atomic gallium have been chosen as best corresponding to the physical and chemical situation in the system.

The problem of describing the liquid phase in the Ga–Pb system thus was reduced to the calculation of activities of lead from the determined activity of gallium. For this purpose we approximated the excess chemical potential of gallium [Eq. (4)] at each temperature by the Margules polynomial [Eq. (5)] [3], selecting the polynomial power *m*.

$$\Delta\mu^E_{Ga} = RT\ln\frac{p_{Ga}}{x_{Ga}p^0_{Ga}}, \tag{4}$$

$$M_m(\alpha_{Ga};x_{Ga}) = (1-x_{Ga})^2\sum_{n=0}^{m-2}\alpha^n_{Ga}(1-x_{Ga})^n. \tag{5}$$

The optimization of interaction parameters for each $2 \le m \le 5$ was carried out by least squares. Selection of *m* was carried out by “manual” minimization according to the condition $R^2_m \ge 0.95$, where R_m is the correlation coefficient.

It turned out that for all investigated temperature range (from 900 to 1170 K) the polynomial power m = 4 was the optimal in this sense, which corresponded to the next approximation after the subregular (three parameters). Therewith, the interaction parameters depend linearly on the temperature according to Eq. (6).

$$\alpha^n_i = \zeta^n_i - \eta^n_i T. \tag{6}$$

Here ζ^n_i is the enthalpy parameter, η^n_i is the entropy parameter, n = 0, 1, 2. The values are shown in the table. Dependences of the interaction parameters of gallium and lead on temperature in the melts of the Ga–Pb system are shown in Fig. 2. Since the total vapor pressure of the system in the temperature range 900–1170 K does not exceed 40 Pa, the conditions of calculations were considered nearly isobaric in the sense that the dependence of the excess potentials on the pressure was neglected. In this approximation, the use of Margules parameters polynomials allowed the calculation of the lead excess potentials with the linear relation (7), where C^n_k are the binomial coefficients, and the calculation of the partial and integral molar functions of mixing.

$$\alpha^n_{Pb} = \sum_{k=n}^{m-2} j_{n,k}\alpha^k_{Ga}, \text{ where } j_{n,k} = (-1)^n\frac{k+2}{n+2}C^n_k. \tag{7}$$

The values of enthalpy (ζ_i^n) and entropy (η_i^n) interaction parameters of Ga and Pb in melts of Ga–Pb system

n	Ga		Pb	
	ζ^n_i, kJ mol^{-1}	η^n_i, J mol^{-1} K^{-1}	ζ^n_i, kJ mol^{-1}	η^n_i, J mol^{-1} K^{-1}
0	139.4	119.8	60.5	36.1
1	–323.2	–307.9	–218.0	–196.3
2	202.9	189.1	202.9	189.1

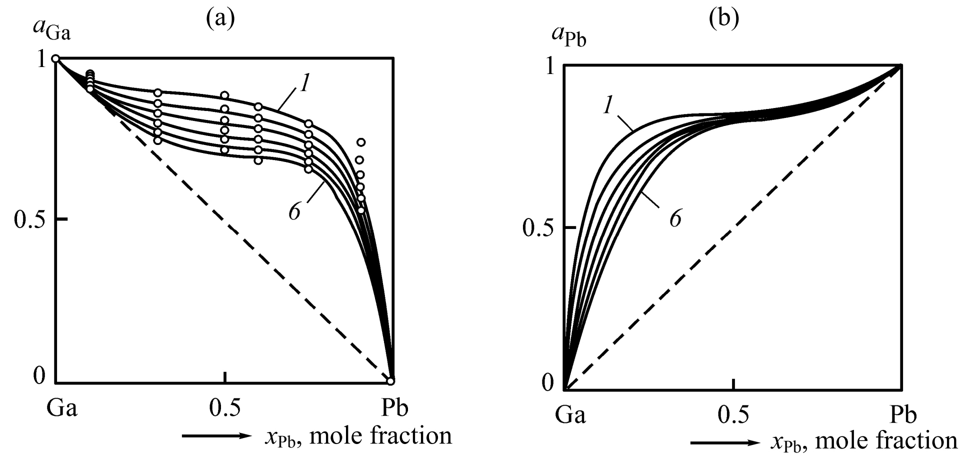

Fig. 3. Dependences of activities of (a) Ga and (b) Pb on condenced phase composition at various temperature: (*1*) 900, (*2*) 950, (*3*) 1000, (*4*) 1050, (*5*) 1110, (*6*) 1170 K. (Points) experimental data, (curves) calculated data.

From the obtained approximations $\Delta\mu_{Ga}^E = M_4(\alpha_{Ga}, x)$, $x \equiv x_{Ga}$, and calculated dependences $\Delta\mu_{Pb}^E = M_4(\alpha_{Pb}, 1 - x)$ using Eq. (8) the curves of the activity of the components were constructed for all the temperatures of the study. Dependences of gallium and lead activities on the composition of the condensed phase at various temperatures are shown in Fig. 3.

$$a_i = x_i \exp\left(\frac{\Delta\mu_i^E}{RT}\right). \quad (8)$$

As seen in Fig. 3, there are strong positive deviations for the components of the melt from ideality, decreasing with increasing temperature. The curves of integral molar excess Gibbs energy ΔG^E and the Gibbs mixing energy ΔG (Fig. 4) are markedly asymmetric, and we can talk about the growing trend towards the disintegration of the liquid phase, expressed as the "flattening" the curve $G = f(x)$ both at low and at high temperatures. With the decreasing temperature, this tendency is enhanced while simultaneously the positive deviations from ideality increase, which then leads to an instability of the liquid phase as seen from the state diagram.

Based on the temperature dependence of the interaction parameters, we calculated the spinodal curve corresponding to the boundary of the internal stability of the liquid phase. As a necessary condition for the stability of a phase of two-component system is non-negative first derivative of the chemical potential on the composition $\partial\mu \geq 0$, for the spinodal curve we can write Eq. (9).

$$\partial\mu_i = \frac{RT}{x_i} + \partial\Delta\mu_i^E(T, x_i) = 0. \quad (9)$$

Here $\partial \equiv \partial/\partial x_i$, i = Ga, Pb. According to the Gibbs–Duhem equation, the potential of any of the components can be used. Substituting the polynomial expression (5) and using the linear dependence of the interaction parameters on the temperature [Eq. (6)], we obtain the spinodal curve [Eq. (10)].

$$T = \frac{x_i \partial M_4(\zeta_i, x_i)}{x_i \partial M_4(\eta_i, x_i) - R}. \quad (10)$$

It turns out that the spinodal of the liquid phase in the Ga–Pb system at the found values of the parameters consists of three branches, and demon-

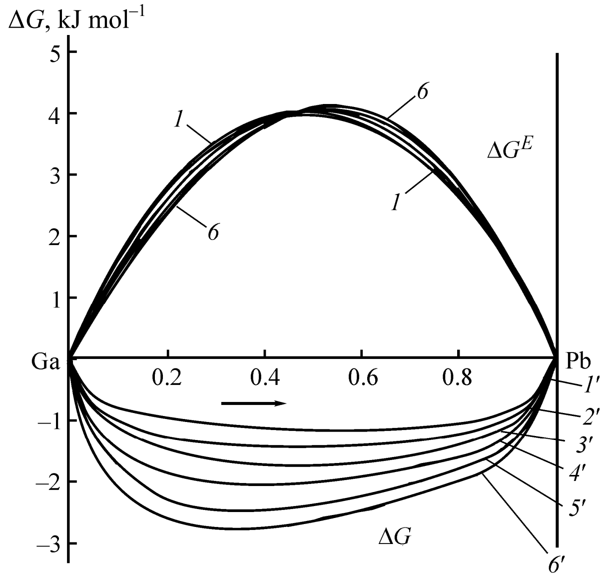

Fig. 4. Dependences of (*1–6*) excess Gibbs energy ΔG^E and (*1′–6′*) Gibbs energy of mixing ΔG melts in the Ga–Pb system on condensed phase composition at various temperatures: (*1*) 900, (*2*) 950, (*3*)1000, (*4*) 1050, (*5*)

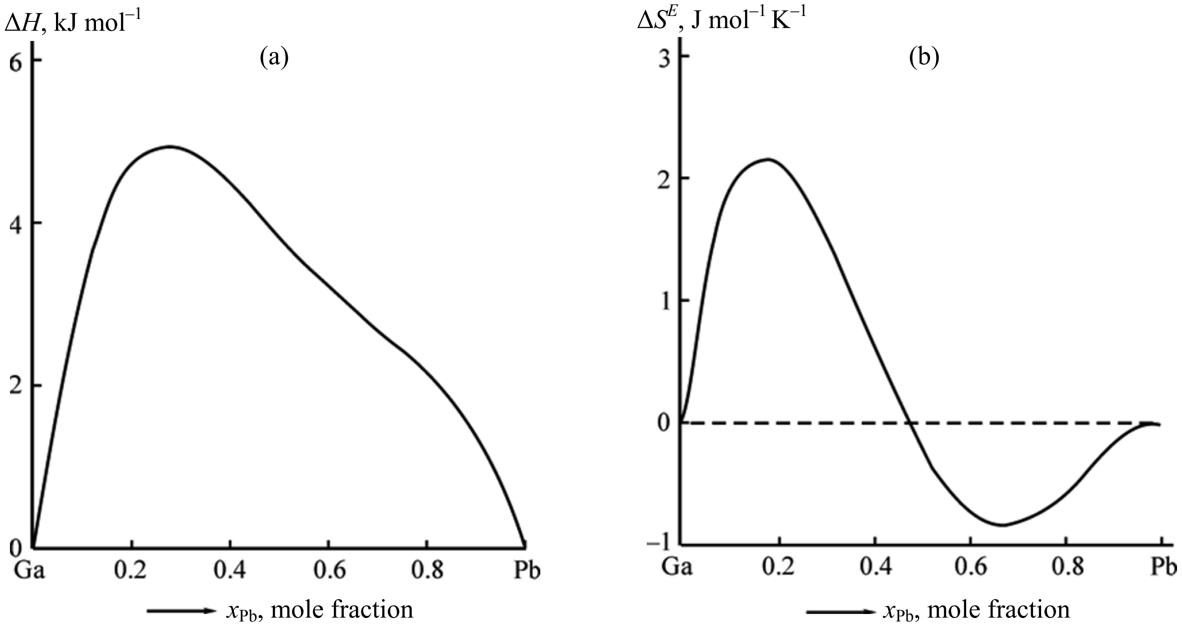

Fig. 5. Dependences of (a) integral enthalpy of mixing and (b) excess entropy of liquid phase components of the Ga–Pb system on the condensed phase composition.

strates the presence of two upper and one lower critical points of the stratification. The first two branches, constructed according to Eq. (10), are shown in Fig. 1 (curves *2* and *3*), and the critical point on the curve *2* corresponds to a temperature of 870.7 K, which is consistent with the state diagram. The third, high-temperature, branch gives the lower critical point 1372 K (not shown in Fig. 1). Since there is no experimental data in this temperature range, it is difficult to judge the validity of this result, however, on the curves $\Delta G = f(x)$ and $a_i = f(x)$ a "flattening" is seen at the high T, together with a decrease in positive deviations from ideality (Figs. 3, 4). As to the second spinodal branch (Fig. 1, curve *3*), it lies in the metastable region below the main binodal curve (Fig. 1, curves *1*, *1'*). It is expected that in the same area lies the binodal corresponding to the second decay of a metastable liquid phase.

Based on the values of enthalpy and entropy parameters (see the table), we calculated partial $\Delta\bar{H}_i$, $\Delta\bar{S}_i^E$ and integral ΔH, ΔS^E molar excess functions of the studied melt. Since the interaction parameters (6) depend linearly on the temperature, the use of the characteristic relations (11a), (11b) shows that these quantities have the same polynomial form (5) as the excess potentials, with the enthalpy and entropy constant replacing the interaction parameters [Eqs. (12a), (12b)].

$$\Delta\bar{H}_i = \Delta\mu_i^E - T\frac{\partial}{\partial T}\Delta\mu_i^E, \tag{11a}$$

$$\Delta\bar{S}_i^E = -T\frac{\partial}{\partial T}\Delta\mu_i^E, \tag{11b}$$

$$\Delta\bar{H}_i = M_4(\zeta_i;x_i), \tag{12a}$$

$$\Delta\bar{S}_i^E = M_4(\eta_i;x_i). \tag{12b}$$

Figure 5 shows the dependences of the thermodynamic functions on the composition of the condensed phase, calculated by Eqs. (13) and (14).

$$\Delta H = x\Delta\bar{H}_{\mathrm{Ga}} + (1-x)\Delta\bar{H}_{\mathrm{Pb}}, \tag{13}$$

$$\Delta S^E = x\Delta\bar{S}_{\mathrm{Ga}}^E + (1-x)\Delta\bar{S}_{\mathrm{Pb}}^E. \tag{14}$$

Note that owing to the constancy of the parameters ζ_i and η_i, these values do not depend on temperature in the studied range. The attention should be drawn to the fact that the function ΔS^E is nonmonotonic. However, the formation of melts in the Ga–Pb system is accompanied by an endothermic heat effect [$\Delta H > 0$ at all $x \in (0, 1)$], and just this enthalpy effect contributes mainly to the positive deviations from ideality. At the point of maximum the ΔH value reaches 4.9 kJ mol^{-1}. Negative ΔS^E values in the range of $0 < x_{\mathrm{Ga}} < 0.525$ reinforce these deviations and contribute additionally to the instability of the liquid phase of the Ga–Pb system.

EXPERIMENTAL

The experimental procedure and data on the partial pressures of vapor components were published in detail in [9]. The measurements were performed on MS-1301 and HERMAG S 40 mass spectrometers. The samples, initially heterophase, were prepared by melting weighed samples of the high purity metals (“0000” EXTRA grade) at a temperature above the monotectic horizontal (670–680 K). Evaporation of the samples of known composition was carried out in a dual one-temperature chamber, using pure lead as a reference sample. In the process of evaporation the change in the sample composition due to selective evaporation of lead was not accounted for, assuming that all data obtained in the temperature range 900–1170 K relate to the given composition.

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