

THERMODYNAMIC ANALYSIS OF THE Ga-Pb BINARY SYSTEM

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Abstract

Thermodynamic properties of binary Ga-Pb alloys were investigated experimentally and analytically. Quantitative differential thermal analysis was used for determination of integral mixing enthalpies for the gallium-rich alloys, at the constant temperature inside the liquid two-phase region. Calculation of gallium activities in the temperature range of 800-1000 K was done using Chou's calculation model developed for binary systems with miscibility gap existence.

Keywords: thermodynamics, quantitative DTA, mixing enthalpy, activity, Ga-Pb liquid alloys

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1. Introduction

Wetting and prewetting phase transitions have been observed recently in some gallium-based systems [1], due to the interest for interfacial phenomena at the surfaces of critical binary liquid mixtures.

Ga-Pb alloys (phase diagram shown in Fig.1 [2]) belong to this group. The phase relationships in this system were investigated by different authors [3, 4], who determined the existence of eutectic and monotectic reaction, as well as a liquid miscibility gap in the greatest part of the composition range.

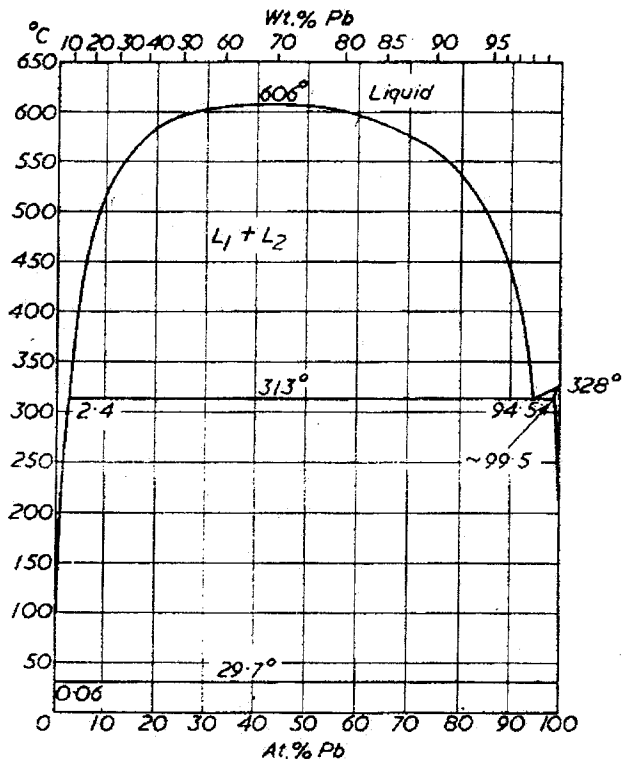


Fig.1. Phase diagram of Ga-Pb system [2]

There are a lot of references on Ga-Pb thermodynamic data [5-12]. Predel and Stein [5] measured integral mixing enthalpies by high-temperature calorimetry, while Bros [6] determined integral mixing enthalpies at 743 K in dilute and gallium-rich alloys. Kwong and Munir [7] performed torsion effusion method in their investigation in the temperature range 950-1050K. Desideri and Piacente [8] determined thermodynamic properties in liquid Ga-Pb system from 1130 to 1160K using vapor pressure measurements, as well as Sommer et al. [9], who gave activities of both components at 1000K. Compilation, of known thermodynamic data for this system (up to 1991), is given by Ansara and Ajaesch [10], while assessment done using a computerized optimization procedure "Parrot" is given in [11]. The most recent research of Ga-Pb system is a paper of Katayama et al. [12], who measured activities of gallium in liquid alloys using emf method with zirconia solid electrolyte in the temperature range 950-1150K.

Although numerous, existing data show some disagreements. Positive deviation for the activities of the constituents is obtained in all cases, but there are important differences between their values due to the experimental technique used or even between results obtained by similar experimental techniques. Also it seems that no thermodynamic data regarding to the liquid miscibility gap area are present in the literature. In the present study quantitative differential thermal analysis was used for determination of integral mixing enthalpies in the composition range $x_{\text{Pb}}=0-0.2$, at the temperature of 601 K which is, according to phase diagram data [2], the area of liquid two-phase region existence. Also, Chou's calculation model [13] for the systems having miscibility gap was applied to determination of gallium activities at the temperatures inside and outside of the liquid two-phase region.

2. Experimental

Quantitative differential thermal analysis [14-16] was used for experimental determination of enthalpies of mixing for liquid Ga-Pb alloys. This technique has been described in details in Ref. [14].

Metals (Ga and Pb) used in this work were of 99.99 mass% purity. The compositions of the experimentally investigated alloys of Ga-Pb system are given in Table 1. The volume of all samples was constant 0.3cm³. The heating

rate in all cases was 10Kmin^{-1} . Calcined alumina was used as reference material.

Table 1. Composition and masses of experimentally investigated Ga-Pb alloys

alloy	x_{Ga}	mass of the alloy (g)
S1	0.8	2.2310
S2	0.85	2.1251
S3	0.9	2.0137
S4	0.95	1.8965
S5	0.975	1.8356

According to the experimental procedure, samples were prepared such that the required gallium mass was melted firstly at the bottom of a pyrex tube, within which a protective tube was fixed for the NiCr-Ni thermocouple. A lead ring of a corresponding mass was fixed to the same tube, in order to provide, after melting, an alloy of the required composition.

Both tubes (with sample and reference material) are heated in the electric resistance furnace according to an appropriate program, so T and ΔT curves could be obtained.

2.1. Theoretical basis

Quantitative differential thermal analysis: The main theoretical principle of DTA application in quantitative calorimetric determination [14-16] is given by the following analytical expression:

$$Q = gK_s \int T dt \quad (1)$$

where are: Q - reaction heat, gK_s - calibration constant of the apparatus and $\int T dt$ - area of DTA peak.

Every measurement run done in this work is characterized by appearance of two peak areas, recorded on single DTA curve. Obtained DTA peak areas are proportional to the corresponding heat effects.

The first DTA peak is due to the heat of melting of the metal with lower

melting point. The total heat absorbed by the sample in the melting process and measured by DTA can be represented as:

$$\Delta H_I = gK_s(M_1)P_1 \quad (2)$$

where: ΔH_I is heat of melting of metal M_1 ; $gK_s(M_1)$ is calibration constant of the apparatus in respect to the metal M_1 ; P_1 is obtained peak area.

The second DTA peak includes two heat effects: heat of melting of metal with higher melting point and heat of mixing of two metals. The total heat effect proportional to the second peak area is:

$$\Delta H_{II} = gK_s(M_2)P_2 + gK_s(\text{alloy})P_{\text{mix}} \quad (3)$$

where: ΔH_{II} is total heat which include heat of melting of metal M_1 and heat of mixing of metals M_1 and M_2 ; $gK_s(M_2)$ is calibration constant of the apparatus in respect to the metal M_2 ; P_2 is obtained peak area due to the heat of melting of metal M_2 ; $gK_s(\text{alloy})$ is calibration constant of the apparatus in respect to the alloy M_1 - M_2 ; P_{mix} is part of second peak area due to the heat of mixing of metals M_1 and M_2 .

Thermodynamic calculation: Chuo's calculation model for the systems having a miscibility gap [13] was applied to determination of gallium activities in the temperature range 800-1000 K. Model is based on phase diagram information about dependence between temperature along the line of the miscibility gap and adequate molar ratio of the investigated binary alloys (in details see Ref. [13]).

3. Results and Discussion

Determination of integral molar enthalpy of mixing: In the first part of applied experimental methodology, functional dependence between peak area and adequate heat effect is established. Calibration constants of the apparatus, gK_s for the pure metals were determined by recording a series of DTA curves for the melting process of pure metals with different masses. Using literature data for enthalpies of melting for gallium (5590 Jmol^{-1}) and lead (4799 Jmol^{-1}) [17], polynomial dependences between melting enthalpies and masses of pure metals were determined.

Linear dependences were calculated by least squares regression analysis and given together with uncertainty limits:

- for lead: $\text{total heat / J} \pm 1.750 = 0.1727 \text{ peak area / mm}^2$
- for gallium: $\text{total heat / J} \pm 1.254 = 0.1017 \text{ peak area / mm}^2$

Determined linear dependences were obtained for pure metals with masses up to 2.5 g. For masses over 2.5 g results were found much more scattered producing bigger deviations. Thus all investigated alloys were used with approximately same volume of 0.3 cm³ and masses smaller of 2.5 g as given in Table 1.

Regarding to already determined fact about existence of a linear dependence of calibration constant on composition for eutectic systems [14], determination of gK_s values for all investigated alloys was done using following relation: $gK_s(\text{Ga-Pb alloy}) = x_{\text{Ga}}gK_s(\text{Ga}) + x_{\text{Pb}}gK_s(\text{Pb})$.

The second part in the quantitative DTA is determination of the integral molar enthalpy of mixing. During the heating of prepared sample gallium melts at its melting point of 303K, which is recorded as the first peak at the obtained DTA curve. Further, as heating process goes on, lead melts at its melting temperature of 600.6 K, and at the same time drops and mixes with melted gallium, which is recorded at the second peak in the obtained DTA curve. The parts of the second peak areas due to lead melting are computed using determined functional dependence between peaks surface and melting heat effect. Those parts were deduced from the overall surfaces of the second peaks to get the contribution of the mixing process.

In order to determine reproducibility and accuracy of the applied method, every experiment was repeated three times. For alloys with higher contents of lead, obtained results for integral molar enthalpies of mixing of Ga-Pb liquid alloys were found more scattered which limited the composition range of investigated system only to gallium rich alloys. Lower degree of reproducibility reached when larger masses of lead were dropping in liquid gallium indicates that the accuracy of the obtained enthalpies of mixing depends of the molar fraction of alloys. Obtained enthalpies of mixing together with the standard deviations are given in Table 2.

Table 2. Integral molar enthalpies of mixing

x_{Ga}	0.8	0.85	0.9	0.95	0.975
$\Delta H^{\text{M}} / \text{Jmol}^{-1}$	1208±195	1152±142	1134±127	1121±98	1046±65

It was found that for all investigated alloys obtained values for integral mixing enthalpies are in the range of 1000-1200 Jmol⁻¹. Very small dependence for integral mixing enthalpies on composition is in accordance with the existence of liquid two-phase region. Results from this work are considerably lower from Predel's values [5] measured at 923 K in liquid single-phase region (maximal value 3853 Jmol⁻¹ for $x_{\text{Ga}}=0.509$) and in relatively good agreement with the results of Bros [6] obtained at 743 K for gallium-rich Ga-Pb alloys.

Several additional factors have also influence on accuracy of the obtained results and have to be pointed out. The effect of inhomogeneous alloying, caused by the difference of densities between two investigated metals and the absence of attraction between the elements, is one among them. Calculated uncertainty limits (obtained in a process of determination of calibration constants for pure metals), together with the approximately taken linear dependence of calibration constant versus the composition, may cause the additional uncertainty in the determined values of enthalpies of formation of the liquid Ga-Pb alloys.

Because of these factors it is considered that the maximal uncertainty in the measured mixing enthalpies was in the region of $\pm 20\%$

Calculation of activities: According to Chou's calculation model and using the phase diagram of Ga-Pb system [2], activity of gallium was calculated in temperature range of 800- 1000K and presented in Tab. 3. Model was tested on temperatures inside and outside of the liquid two-phase region. The critical temperature in this system is 879 K, which means that activities of gallium calculated at the temperatures below the critical point and in the composition range corresponding to the two-phase region should have constant values. Therefore, calculated results at 800 K and 850 K were analyzed regarding to the phase diagram. At 850 K, calculated activity of gallium in the composition range $x_{\text{Ga}}=0.35-0.85$ was found nearly constant which is in the reasonable

agreement with the phase diagram data. At 800 K gallium activity values do not have similar tendency and composition range with constant gallium activity corresponding to the liquid two-phase region was not noticed. At temperatures lower than 800 K calculated activity values for gallium were found to be greater than unity in the certain composition intervals. These results could not be useful for further assessment of this system and are not shown in the present paper.

Table 3. Calculated activities of gallium at different temperatures

x_{Ga}	a_{Ga}			
	800 K	850 K	900 K	1000 K
0	0	0	0	0
0.1	0.641	0.547	0.480	0.386
0.2	0.914	0.81	0.722	0.610
0.3	0.978	0.886	0.810	0.704
0.4	0.976	0.905	0.850	0.767
0.5	0.955	0.905	0.862	0.801
0.6	0.931	0.901	0.867	0.826
0.7	0.914	0.893	0.876	0.850
0.8	0.905	0.895	0.888	0.875
0.9	0.921	0.921	0.919	0.917
1	1	1	1	1

For the results inside of single-phase region, calculated activity of gallium at 1000 K is compared with the results of Katayama *et al.* [12] at Fig. 2. and good mutual agreement is noticed.

Based on the results of this analysis it could be concluded that successful applicability of this calculation model to Ga-Pb binary system lies in the temperature range of single-phase region and at the temperatures in the two-phase region very close to the critical temperature.

4. Conclusions

Using quantitative DTA integral mixing enthalpies of Ga-Pb liquid alloys

at the melting temperature of lead and in the composition range of $x_{\text{Pb}}=0-0.2$ were obtained. The obtained heat effects of mixing are very small and values are very close to each other, which correspond to the existence of liquid two-phase domain. For the alloys with higher content of lead no satisfactory accuracy and reproducibility of the results was reached which limited experimental investigations only to gallium rich alloys. Calculation method developed for the systems with the miscibility gap was used for calculation of gallium activities at different temperatures inside and outside of the miscibility gap. Calculated activities of gallium in the liquid single-phase region are in the good agreement with the latest experimental results. Calculated activities in the miscibility gap region correspond to the phase diagram data only at the temperatures close to the critical one.

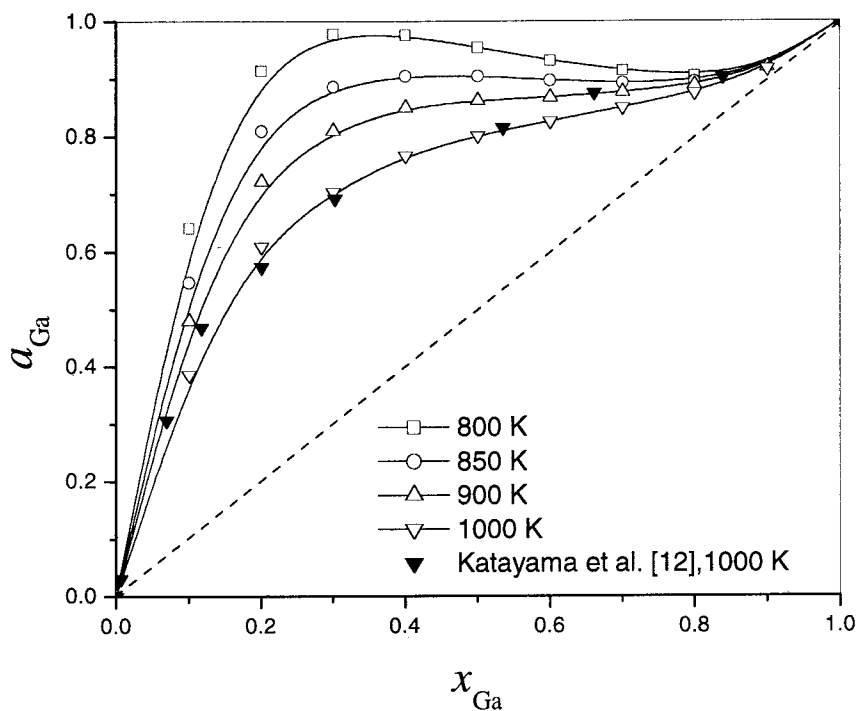


Fig. 2. The activity of gallium at different temperatures

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