

## Calculation of activities in some gallium-based systems with a miscibility gap

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*Abstract:* The calculations of thermodynamic properties in some gallium-based systems with a miscibility gap – Ga–Tl, Ga–Hg and Ga–Pb are presented in this paper. The determination of the gallium activities in the mentioned liquid alloys was based on their known phase diagrams using the Zhang-Chou method for calculating activities from phase diagrams involving two liquid or solid coexisting phases. The activities of gallium in Ga–Tl, Ga–Hg and Ga–Pb system were calculated in the 973–1273 K, 573–873 K and 1000–1100 K, temperature ranges, respectively. The activities of the other component in all the investigated systems were obtained by the Gibbs-Duhem equation. The results of the calculations are compared with literature data.

*Keywords:* thermodynamic calculation, Ga–Tl, Ga–Hg, Ga–Pb systems, phase diagrams, miscibility gap.

### INTRODUCTION

There is a fundamental relationship between thermodynamic properties and phase diagrams. From this point of view, due to the great efforts of the CALPHAD (CALculation of PHase Diagrams) research group,<sup>1</sup> this scientific area has been developed to a very high level.

Calculation of activities from binary phase diagrams, which has progressed during the past few decades,<sup>2</sup> is one of the methods for obtaining activity data. This is very important from the scientific and technological point of view, because correct determination of thermodynamic properties for binary systems presents a starting point for the calculation of phase diagrams of more complex, multi-component systems.

Many methods for different types of binary phase diagrams have been developed so far. In this sense, the work of Chou and his coworkers<sup>2</sup> should be specially emphasized. In a series of papers,<sup>3–6</sup> Chou developed a significant number of methods for the calculation

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of thermodynamic properties based on different types of binary phase diagrams. Besides the known phase diagrams of investigating alloys, for the derivation of formulae in some of the methods, Chou used the Richardson assumption – a semi-empirical equation with a relatively long history in the literature.<sup>7-9</sup>

In this work one of these calculation methods, developed for systems with two coexisting liquid or solid phases,<sup>6</sup> has been used for the determination of thermodynamic properties for gallium in some gallium-based binary systems with the existence of a liquid miscibility gap.

#### THEORETICAL BASIS

The representative part of the phase diagram, typical for miscibility gap existence, used for the calculations done in this work is shown in Fig. 1.

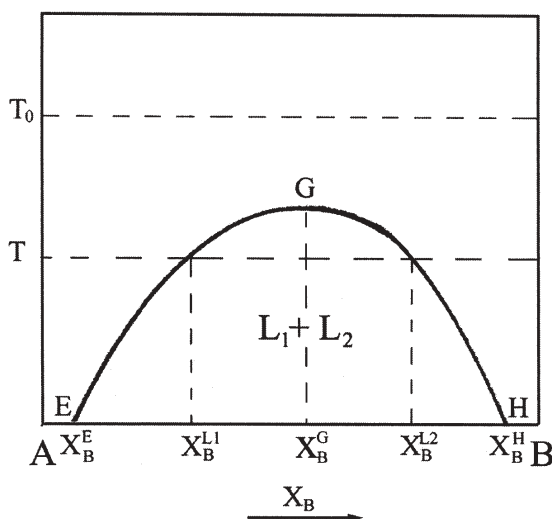


Fig. 1. The representative part of the phase diagram A-B.

In the composition interval involving two coexisting liquid phases ( $L_1 + L_2$ ), the activities of component A can be obtained as follows:<sup>6</sup>

From  $x_B = x_B^E$  to  $x_B = x_B^G$ , the formula for the calculation of the activity coefficient of component A is given as:

$$\ln \gamma_{A(x_A^{L_1}, T_0)} = \ln \gamma_{A(x_A^E, T_0)} + \int_{\frac{\sigma}{\sigma_0} x_B^{L_1}}^{\frac{\sigma}{\sigma_0} x_B^{L_2}} \frac{1}{x_B^{L_1} - x_B^{L_2}} [x_B^{L_1 \Sigma L_2} - x_B^{L_2 \Sigma L_1}] d\left(\frac{\sigma}{\sigma_0}\right) - \left(\frac{\sigma}{\sigma_0} \ln x_A^{L_1} - \frac{\sigma_E}{\sigma_0} \ln x_A^E\right) \quad (1)$$

and in the composition interval from  $x_B = x_B^G$  to  $x_B = x_B^H$ :

$$\ln \gamma_{A(x_A^{L_2}, T_0)} = \ln \gamma_{A(x_A^{L_1}, T_0)} - \frac{\sigma}{\sigma_0} \ln \frac{x_A^{L_2}}{x_A^{L_1}} \quad (2)$$

where  $\gamma_{A(x_A^{L_1}, T_0)}$ : the activity coefficient of component A at the temperature  $T_0$  and  $x_A^{L_1}$  mole fraction;  $\gamma_{A(x_A^E, T_0)}$ : the activity coefficient of component A at the temperature  $T_0$  and  $x_A^E$  mole fraction;  $\gamma_{A(x_A^{L_2}, T_0)}$ : the activity coefficient of component A at temperature  $T_0$  and  $x_A^{L_2}$  mole fraction and:

$$\Sigma^{L_1} = x_A^{L_1} \ln x_A^{L_1} + x_B^{L_1} \ln x_B^{L_1} \quad (3)$$

$$\Sigma^{L_2} = x_A^{L_2} \ln x_A^{L_2} + x_B^{L_2} \ln x_B^{L_2} \quad (4)$$

$$\sigma_E = \frac{T_E}{1 - \frac{T_E}{\theta}} \quad (5)$$

where  $T_E$  is temperature at point "E" (Fig. 1).

$$\sigma = \frac{T}{1 - \frac{T}{\theta}} \quad (6)$$

where  $T$  is the variable temperature at the line of the miscibility boundary (Fig. 1).

$$\sigma_0 = \frac{T_0}{1 - \frac{T_0}{\theta}} \quad (7)$$

where  $T_0$  is a fixed temperature in the liquid single phase region (Fig. 1).

$$\theta = \frac{H_i}{S_i^E} = 3000 \text{ K (Richardson assumption)} \quad (8)$$

Equation (1) can be solved if the phase diagram of the investigated system and the activity coefficient of component A in the investigated temperature  $T_0$  for  $x_A^E$  mole fraction are known. If at the bottom of the two phase region near the terminat rich in componenet A (point E in Fig. 1) the mole fraction of component B is close to zero, the activity coefficient of componenet A ( $\gamma_{A(x_A^E, T_0)}$ ) can be approximately used as being equal to unity, as was done in this work for the determination of the gallium activities. The integral term in Eq. (1) can be determined by graphical integration.

An analogous set of equations can be derived in the case of component B.<sup>6</sup>

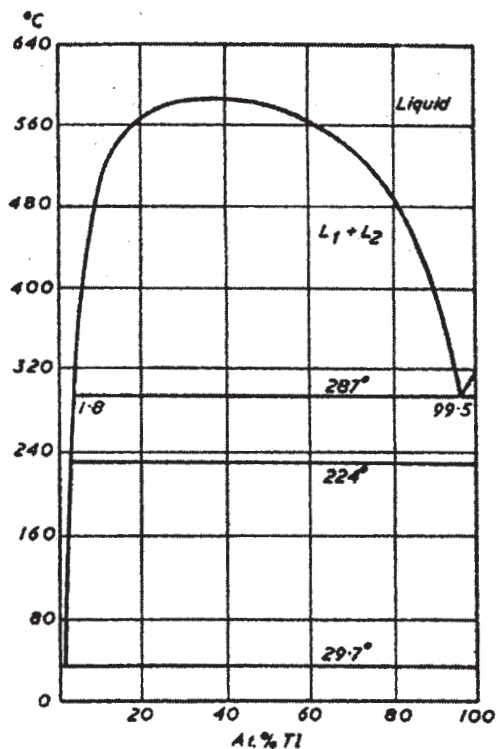


Fig. 2. The Ga-Tl phase diagram.

After the determination of the activities of component A over the entire composition interval, the activities of component B can be derived using the Gibbs-Duhem equation and the  $\alpha$ -function:

$$\ln a_B = \ln x_B - x_A x_B \alpha_A + \int_0^{x_A} \alpha_A dx_A \quad (9)$$

$$\alpha_A = \frac{\ln \gamma_A}{(1 - x_A)^2} \quad (10)$$

where  $\gamma$  is the activity coefficient and  $x$  is the mole fraction.

## RESULTS AND DISCUSSION

### a) Ga-Tl system

The phase diagram of the Ga-Tl system,<sup>10</sup> used for the calculation, is shown in Fig. 2. Two extreme end points E and H at the bottom of the two coexisting liquid phase region at a temperature of 560 K are  $x_{Tl}^E = 0.018$  and  $x_{Tl}^H = 0.995$ , respectively.

In the composition range from  $x_{Tl} = 0.018$  to  $x_{Tl} = 0.995$ , the activities of gallium in the temperature interval 973–1273 K, calculated by Eqs. (1) and (2), are listed in Table I.

Based on the calculated activities of gallium, the activities of thallium were calculated using Eqs. (9, 10). All the obtained results for thallium activities are also shown in Table I.

TABLE I. Calculated activities of gallium and thallium for the chosen alloys at different temperatures

$x_{\text{Ga}}$	$x_{\text{Tl}}$	973 K		1073 K		1173 K		1273 K	
		$a_{\text{Ga}}$	$a_{\text{Tl}}$	$a_{\text{Ga}}$	$a_{\text{Tl}}$	$a_{\text{Ga}}$	$a_{\text{Tl}}$	$a_{\text{Ga}}$	$a_{\text{Tl}}$
0.1	0.9	0.383	0.945	0.320	0.941	0.274	0.935	0.241	0.931
0.2	0.8	0.586	0.900	0.504	0.872	0.450	0.863	0.407	0.854
0.3	0.7	0.701	0.824	0.625	0.802	0.565	0.787	0.523	0.775
0.4	0.6	0.767	0.782	0.701	0.753	0.651	0.732	0.612	0.712
0.5	0.5	0.801	0.757	0.75	0.718	0.713	0.689	0.677	0.660
0.6	0.4	0.828	0.758	0.795	0.677	0.762	0.635	0.74	0.596
0.7	0.3	0.852	0.710	0.829	0.619	0.811	0.563	0.795	0.519
0.8	0.2	0.875	0.616	0.864	0.543	0.856	0.476	0.849	0.426
0.9	0.1	0.916	0.464	0.913	0.390	0.912	0.325	0.910	0.279

A complete review of the obtained results is given in Fig. 3.

The calculated activities of gallium at 973 and 1073 K are compared with the experimental results of Katayama *et al.*<sup>11</sup>, obtained by the emf method with zirconia as the solid electrolyte, in Fig. 4.

Good agreement can be noticed between the calculated and experimental results. Positive deviations from the ideal solution law, characteristic for systems with a miscibility gap present in liquid phase, were obtained for all investigated temperatures.

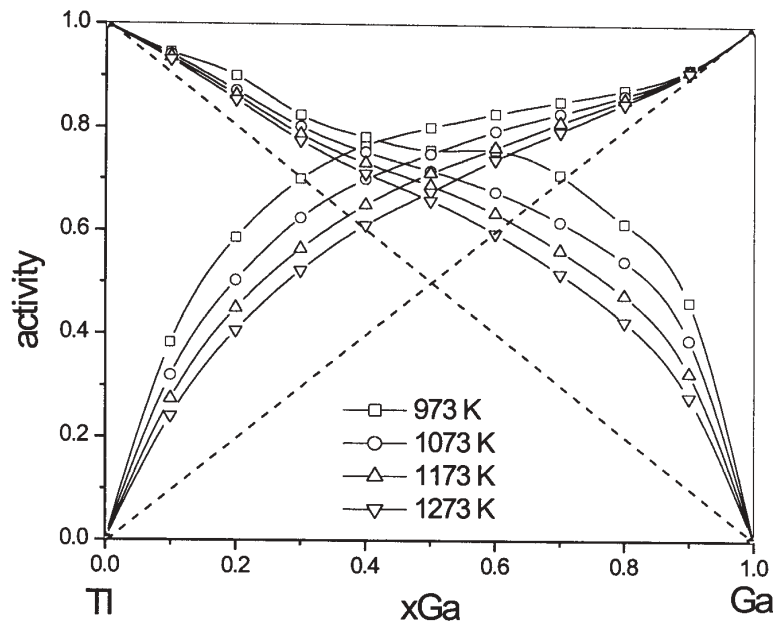


Fig. 3. Activities of gallium and thallium at different temperatures.

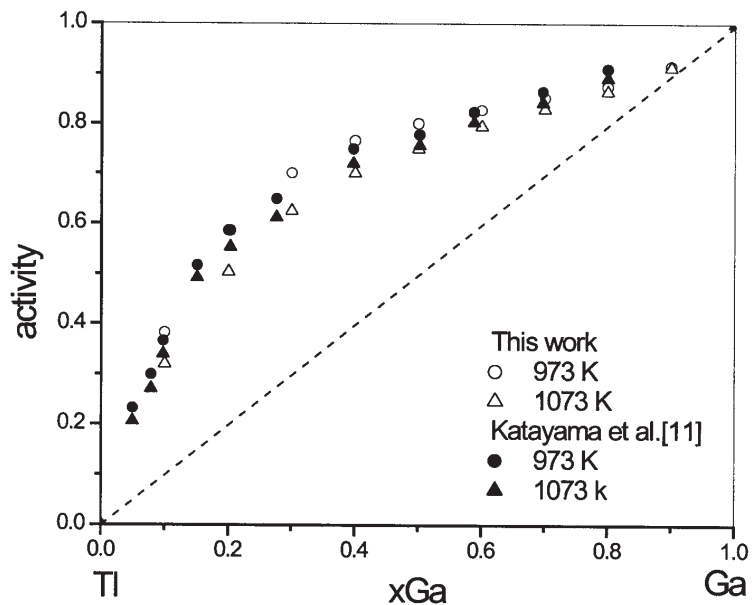


Fig. 4. Comparison between the calculated and experimental values of the gallium activities at different temperatures.

b) Ga–Hg system

The phase diagram of the Ga–Hg system<sup>10</sup> is shown in Fig. 5.

For the Ga–Hg binary system, a large coexisting liquid phase region is also involved.

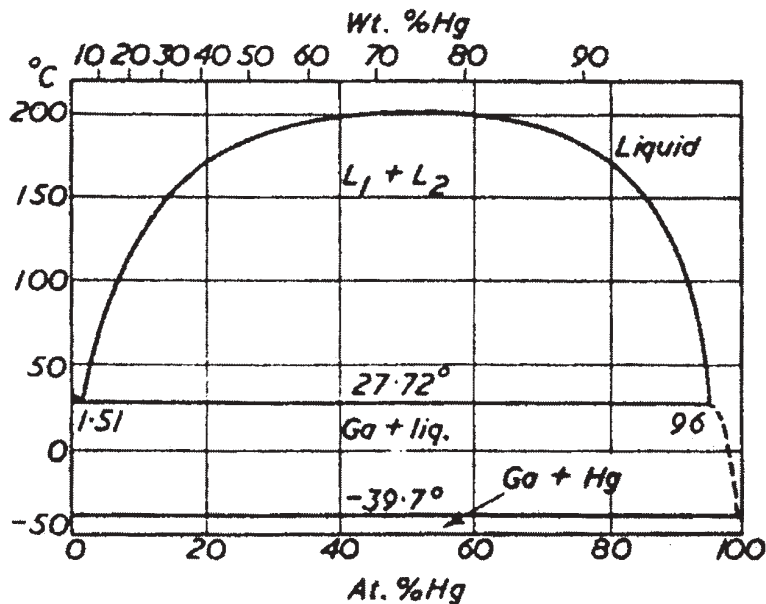


Fig. 5. The Ga–Hg phase diagram.

The composition of the two extreme terminals at the bottom of the two coexisting phase region are  $x_{\text{Hg}}^{\text{E}} = 0.0151$  and  $x_{\text{Hg}}^{\text{H}} = 0.96$ , respectively.

Employing the same procedure used in the example of the Ga–Tl system, the activities of gallium and mercury were calculated, and the obtained results are listed in Table II.

TABLE II. Calculated activities of gallium and mercury for the chosen alloys at different temperatures

$x_{\text{Ga}}$	$x_{\text{Hg}}$	573 K		673 K		773 K		873 K	
		$a_{\text{Ga}}$	$a_{\text{Hg}}$	$a_{\text{Ga}}$	$a_{\text{Hg}}$	$a_{\text{Ga}}$	$a_{\text{Hg}}$	$a_{\text{Ga}}$	$a_{\text{Hg}}$
0.1	0.9	0.398	0.915	0.307	0.912	0.253	0.910	0.214	0.909
0.2	0.8	0.604	0.856	0.493	0.842	0.424	0.836	0.378	0.830
0.3	0.7	0.692	0.813	0.589	0.794	0.528	0.776	0.483	0.766
0.4	0.6	0.74	0.797	0.66	0.755	0.607	0.726	0.569	0.705
0.5	0.5	0.771	0.770	0.710	0.706	0.670	0.670	0.634	0.64
0.6	0.4	0.805	0.722	0.762	0.648	0.732	0.599	0.710	0.562
0.7	0.3	0.836	0.665	0.808	0.579	0.789	0.518	0.775	0.477
0.8	0.2	0.872	0.592	0.857	0.486	0.848	0.417	0.840	0.373
0.9	0.1	0.926	0.400	0.920	0.314	0.916	0.257	0.914	0.224

All the obtained results are shown in Fig. 6.

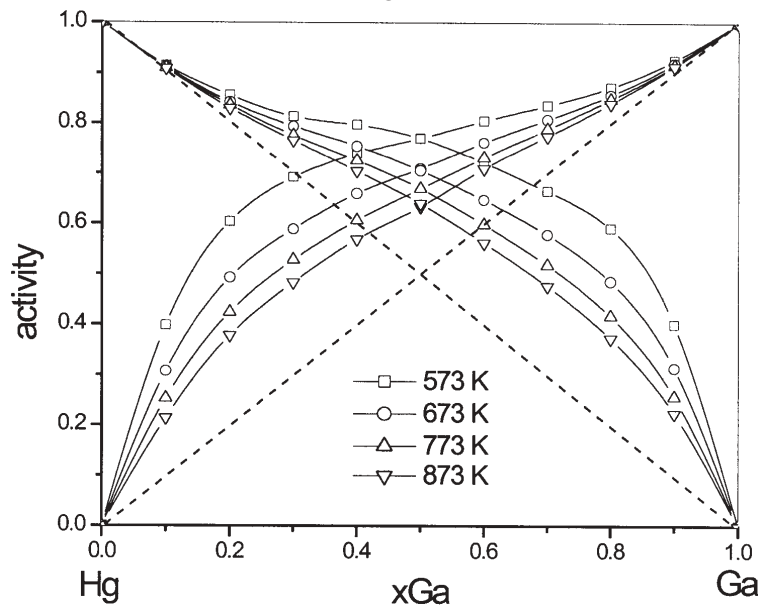


Fig. 6. Activities of gallium and mercury at different temperatures.

The results obtained in this work are compared with the results of the Guminski and Zabdyr study of the Ga–Hg system.<sup>12</sup> In their study, the available experimental data for the liquid phase of the Ga–Hg binary system were critically evaluated and expressed in the polynomial formula for the integral excess Gibbs energy of mixing, which is for an  $ij$  bi-

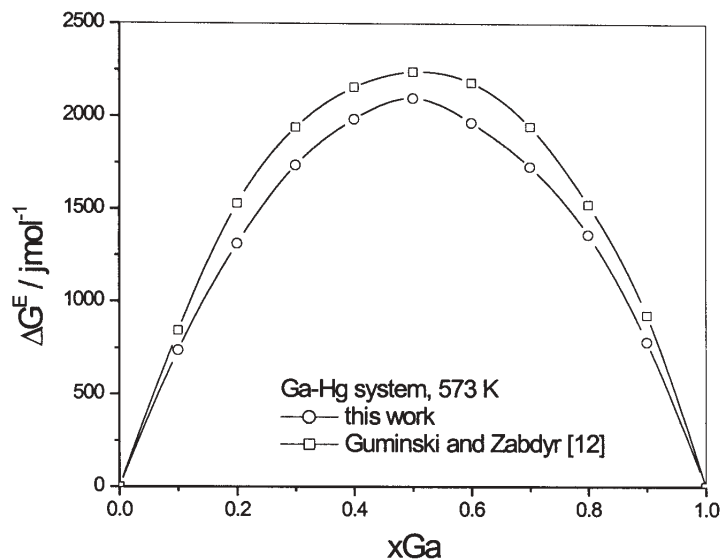


Fig. 7. Excess Gibbs energies of liquid Ga-Hg alloys.

nary system defined as:

$$\Delta G_{ij}^E = RT(x_i \ln \gamma_i + x_j \ln \gamma_j)$$

where  $\gamma$  represents the activity coefficient.

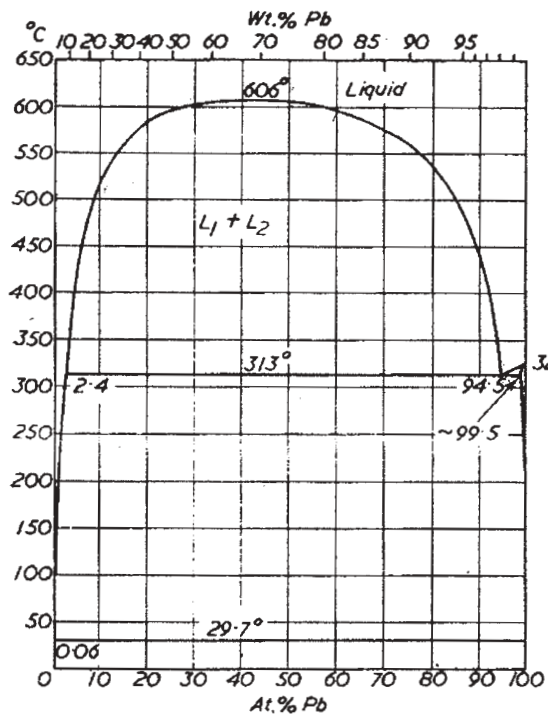


Fig. 8. The Ga-Pb phase diagram.



Mutual comparison was done at 573 K and presented in Fig. 7.

Very good agreement can be noticed. As in case of the Ga–Tl system, significant positive deviation from ideal solution behavior indicates very poor mixing capability between gallium and mercury in the liquid phase.

c) Ga–Pb system

The phase diagram of Ga–Pb system<sup>10</sup> is shown in Fig. 8.

For the Ga–Pb binary system, the composition of two extreme terminals at the bottom of the two coexisting phase region are  $x_{\text{Pb}}^{\text{E}} = 0.024$  and  $x_{\text{Pb}}^{\text{H}} = 0.945$ , respectively.

The calculated values are presented in Table III.

The calculated activities of gallium and lead are compared with the results obtained by the emf measurements with zirconia as the solid electrolyte of Katayama *et al.*<sup>13</sup> in Fig. 9.

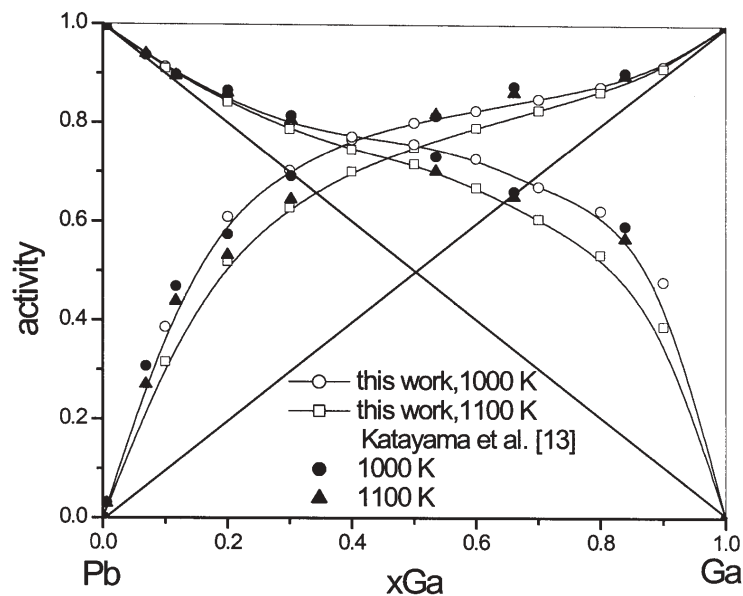


Fig. 9. Activities of gallium and lead at different temperatures.

The comparison with the experimental results shows good mutual agreement.

TABLE III. Calculated activities of gallium and lead for the chosen alloys at different temperatures.

$x_{\text{Ga}}$	$x_{\text{Pb}}$	1000 K		1100 K	
		$a_{\text{Ga}}$	$a_{\text{Pb}}$	$a_{\text{Pb}}$	$a_{\text{Ga}}$
0.1	0.9	0.386	0.913	0.316	0.911
0.2	0.8	0.610	0.846	0.519	0.842
0.3	0.7	0.704	0.798	0.628	0.787

TABLE III. Continued

$x_{\text{Ga}}$	$x_{\text{Pb}}$	1000 K		1100K	
		$a_{\text{Ga}}$	$a_{\text{Pb}}$	$a_{\text{Pb}}$	$a_{\text{Ga}}$
0.4	0.6	0.767	0.772	0.702	0.746
0.5	0.5	0.801	0.757	0.751	0.717
0.6	0.4	0.826	0.728	0.791	0.670
0.7	0.3	0.85	0.671	0.827	0.606
0.8	0.2	0.875	0.623	0.864	0.533
0.9	0.1	0.917	0.479	0.913	0.388

## CONCLUSION

A method for calculating the activities from phase diagrams involving two liquid or solid coexisting phases was applied to the Ga–Tl, Ga–Hg and Ga–Pb binary systems. The activities of the components in the liquid phase, for all the investigated systems, were determined over wide temperature ranges. Positive deviation from ideal solution behavior was noticed in all cases. The activities significantly decrease with increasing temperature in every system. The results for Ga–Tl and Ga–Pb systems are compared with those obtained by emf measurements with a zirconia solid electrolyte. Good mutual agreement between the calculated and experimental results for all the investigated systems indicates the possibility for the efficient application of this method to other systems with miscibility gap existence.

## ИЗВОД

## ПРОРАЧУН АКТИВНОСТИ У БИНАРНИМ СИСТЕМИМА НА БАЗИ ГАЛИЈУМА СА ПОСТОЈАЊЕМ ПРЕКИДА РАСТВОРЉИВОСТИ У ТЕЧНОМ СТАЊУ

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У овом раду изложен је прорачун термодинамичких величина у бинарним легурама на бази галијума (Ga–Tl, Ga–Hg и Ga–Pb). Активности у наведеним системима су прорачунате на основу познатих фазних дијаграма коришћењем Zhang–Chou-ове методе развијене за бинарне системе са прекидом растворљивости у течном стању. Активности галијума у функцији састава за Ga–Tl, Ga–Hg и Ga–Pb системе у температурним интервалима 973–1273 K, 573–873 K и 1000–1100 K, респективно, су добијене применом наведене методе, док је за одређивање активности друге компоненте у сваком од наведених система коришћена Gibbs–Duhem-ова једначина. Сви добијени резултати су упоређени са литературним експерименталним резултатима новијег датума и показују добро слагање са њима.

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