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Thermodynamic analysis of binary systems Ge–Ga and Ge–Sb

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Abstract

Results of experimental thermodynamic analysis of binary systems Ge–Ga and Ge–Sb obtained by Oelsen calorimetry are presented in this paper. Activities, activity coefficients, partial molar quantities for both components in the investigated systems at temperatures 1073, 1173 and 1273 K are determined. Also, integral mixing enthalpies in the temperature interval 350–1300 K are determined and given in the enthalpy isotherm diagram. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Alloy thermodynamics; Oelsen calorimetry; Binary systems Ge–Ga and Ge–Sb

1. Introduction

Binary systems Ge–Ga and Ge–Sb are of the importance in the industry of semiconducting materials [1,2]. The knowledge of their special characteristics is necessary for the further progress in electronics, because of their use in the optical and electronical devices as materials for transistors, optical cables, semiconductors, integrated circuits, etc. [2].

There are no so many thermodynamic data for binary systems Ge–Ga and Ge–Sb in literature [3–10]. Namely, for binary system Ge–Ga, in reference [3] heats of formation were determined, also, enthalpy of mixing was determined in [4,6,7], excess entropy in [3,4,6,7] and free energy of mixing at 1240 K in [6]. For binary system Ge–Sb, activities for both components at 1273 K were determined in [9] and enthalpy of mixing in [10].

For that reason, full thermodynamic description and determination of the thermodynamic properties of those systems are important from the scientific and practical point of view.

In this paper, Oelsen calorimetry was used for thermodynamic description and determination of the binary systems Ge–Ga and Ge–Sb, known in literature [11–13] as an efficient method for the thermodynamic analysis of binary and multi-component systems.

In such a way, thermodynamic data for binary systems Ge–Ga and Ge–Sb are completed and possibilities were made for studying multi-component systems in which those binary systems participate.

2. Experimental

All experimental investigations were carried out with pure germanium, gallium and antimony of p.a. grade.

Oelsen calorimetry was used for the thermodynamic analysis of the binary systems Ge–Ga and Ge–Sb.

Oelsen calorimetry can be successfully used for investigation of metallic systems, and gives satisfac-

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Table 1
Composition of the investigated samples

SYSTEM Ge–Ga

No.	Composition (wt%)		Molar content		Mass (g)		Total mass (g)
	Ge	Ga	x_{Ge}	x_{Ga}	Ge	Ga	
A1	0	100	0	1	0	5.91	5.9100
A2	0.006	99.994	0.0001	0.9999	0.0004	5.9096	5.9100
A3	20	80	0.1936	0.8064	1.1564	4.6254	5.7818
A4	40	60	0.3903	0.6097	2.2636	3.3954	5.6590
A5	60	40	0.5903	0.4097	3.3248	2.2165	5.5413
A6	80	20	0.7934	0.2066	4.3427	1.0857	5.4284
A7	100	0	1	0	5.3200	0	53200

SYSTEM Ge–Sb

No.	Composition (wt%)		Molar content		Mass (g)		Total mass (g)
	Ge	Sb	x_{Ge}	x_{Sb}	Ge	Sb	
B1	0	100	0	1	0	6.6800	6.6800
B2	9.2	90.8	0.1452	0.8548	0.6004	5.9261	6.5265
B3	10	90	0.1571	0.8429	0.6513	5.8621	6.5134
B4	20	80	0.2954	0.7046	1.2710	5.0841	6.3551
B5	40	60	0.5279	0.4721	2.4241	3.6362	6.0603
B6	60	40	0.7156	0.2844	3.4750	2.3167	5.7917
B7	100	0	1	0	5.3200	0	5.3200

tory results [12,13]. For that reason, this method is used in this paper.

Descriptions of this experimental technique are reported in literature [11–13].

Seven samples with determined composition and constant volume of 1 cm^3 for each system were chosen for further experimental investigation.

Their composition is given in Table 1.

The examined samples were heated about 100 K above researched temperature. After achieving researched temperature, the test-tube with samples were put from furnace to calorimeter and the temperature of water in calorimeter was read every 30 s. From the cooling curves temperatures of samples was registered.

The water equivalent was determined by a standard method using dissolved Na_2CO_3 and it has a value of 3453 JK^{-1} for the used calorimeter.

3. Results and discussion

Based on the cooling curves obtained by rapid cooling of investigated samples in Oelsen calorimeter, the phase diagram of the investigated binary systems Ge–Ga and Ge–Sb were obtained and are shown in Fig. 1. The experimental data show good agreement with literature data [14,15].

In Oelsen thermodynamic analysis [11] thermodynamic properties are determined by so-called Oelsen integral, which enable calculating partial molar Gibbs energy of mixing from directly measured values of enthalpies, and, like this, activities of the components of the system.

If the binary eutectic system A–B concerns for alloy with composition $x_B = x$ at temperature T, the integral Gibbs mixing energy will be:

$$\Delta G^{M}_{x,T} = (1-x)G^{M}_{A,T} + xG^{M}_{B,T}. \tag{1}$$

If the relationship between partial molar Gibbs mixing energy and activity

$$\Delta G^{M}_{x,T} = (1-x)RT\ln a_{A,T} + xRT\ln a_{B,T} \tag{2}$$

takes and, on the other hand, according to Gibbs–Helmholtz equation

$$\Delta G^{M}_{x,T} = \Delta H^{M}_{x,T} + T\Delta S^{M}_{x,T} \tag{3}$$

it will follow that:

$$\Delta H^{M}_{x,T} - T\Delta S^{M}_{x,T} = (1-x)RT\ln a_{A,T} + xRT\ln a_{B,T}. \tag{4}$$

In Oelsen thermodynamic analysis [11], determination of activities of the components in the system is conceived on knowledge of enthalpy and entropy article. In condition of equilibria and constant

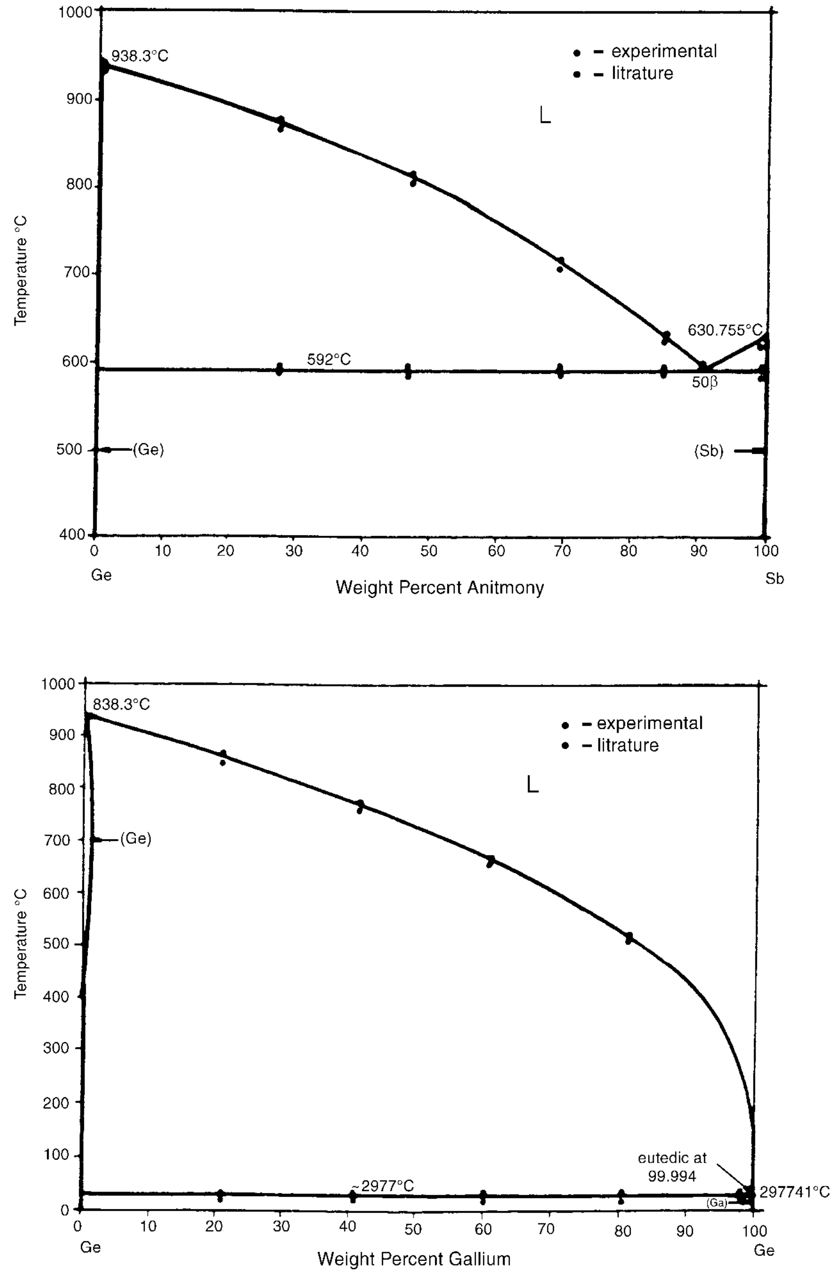

Fig. 1. The phase diagrams of binary systems Ge–Ga and Ge–Sb.

pressure, the entropy article can be written as:

$$\mathrm{d}S^{\mathrm{M}}_{x,T} = \mathrm{d}H^{\mathrm{M}}_{x,T}/T, \tag{5}$$

whereas:

$$S^{\mathrm{M}}_{x,T} = S^{\mathrm{M}}_{x,T=0} + \int_{H_{x,T=0}}^{H^{\mathrm{M}}_{x,T}} \mathrm{d}H^{\mathrm{M}}_{x,T}/T. \tag{6}$$

If we use Nernst theorem, $S^{\mathrm{M}}_{x,T} = 0$, the following expression could be given as:

$$S^{\mathrm{M}}_{x,T} = \int_{H^{\mathrm{M}}_{x,T=0}}^{H^{\mathrm{M}}_{x,T}} \mathrm{d}H^{\mathrm{M}}_{x,T}/T. \tag{7}$$

By Eqs. (4) and (7), follows next relation:

$$\Delta G^{\mathrm{M}}_{x,T} = H^{\mathrm{M}}_{x,T} - T\int_{H^{\mathrm{M}}_{x,T=0}}^{H^{\mathrm{M}}_{x,T}} \mathrm{d}H^{\mathrm{M}}_{x,T}/T. \tag{8}$$

Because of better survey, Oelsen introduced the mark $I_{x,T}$, which represented the measured value of enthalpy that is directly determine in calorimeter, or:

$$I_{x,T} = H^{\mathrm{M}}_{x,T} - H^{\mathrm{M}}_{x,V},, \tag{9}$$

where V is room temperature 298 K. Multiplying the Eq. (8) with (−T) and using expression (9), we have got:

$$-G^{\mathrm{M}}_{x,T}/T = \int_{I_{x,V}}^{I_{x,T}} \mathrm{d}I_{x,T}/T - \int_{1/V}^{1/T} I_{x,T}\mathrm{d}(1/T) \tag{10}$$

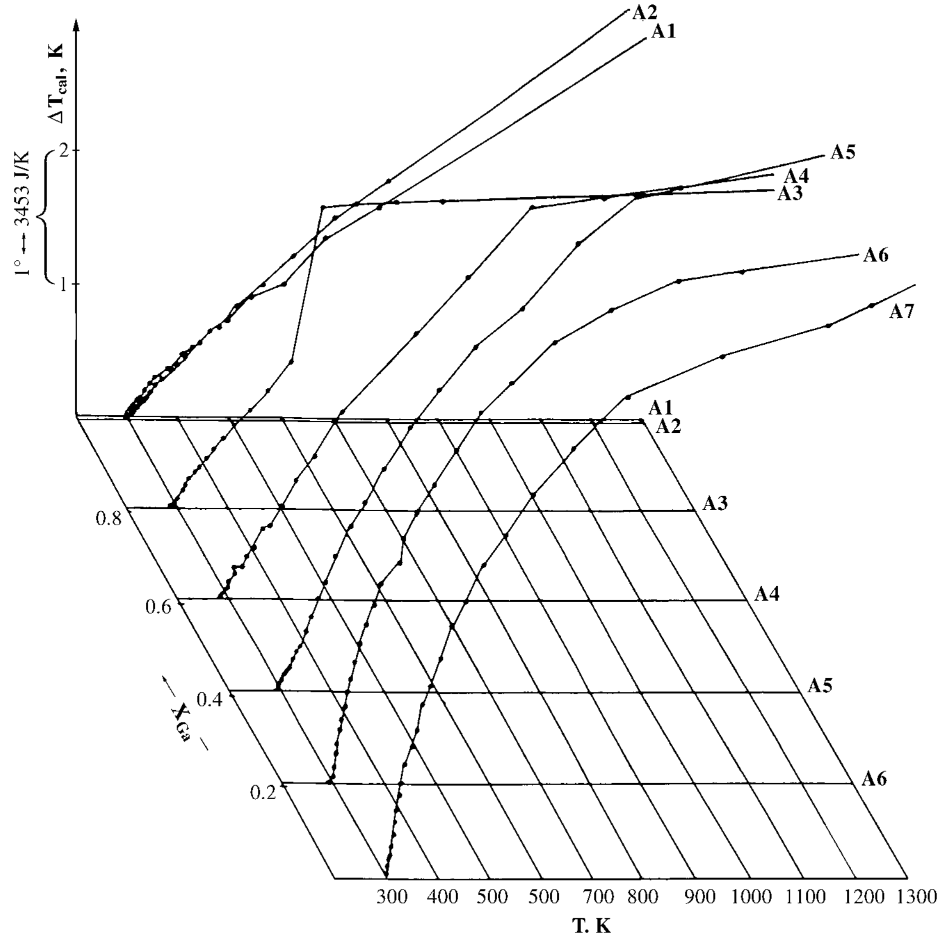

Fig. 2. The space diagram: the temperature change of the calorimetric vs. molar content and temperature for the binary system Ge–Ga.

which represented important Oelsen integral. This Oelsen integral enables determination partial molar Gibbs mixing energy by directly measured values of enthalpies, i.e. according to relationship $G_i^{\mathrm{M}} = RT\ln a_i$ and activity of component. Solution of Oelsen integral is done by graphical method of planimetry areas below cooling curves.

Therefore, the basic equation used in Oelsen thermodynamic analysis is:

$$-G_i^{\mathrm{M}}/T = \int_{1/T_0}^{1/T} H_{x,T}\mathrm{d}(1/T) = -R\ln a_i, \quad (11)$$

where G_i^{M} is the partial Gibbs energy for component i, T_0 is the starting temperature, T the finite temperature, $H_{x,T}$ the enthalpy value measured in the Oelsen calorimeter for the temperature change from T_0 to T, R the gas constant and a_i the activity of the component i.

The first step in Oelsen thermodynamic analysis is the construction of the space-diagram dependence of the temperature change of the calorimeter upon molar content and temperature. These are shown for binary systems Ge–Ga and Ge–Sb in Fig. 2 and Fig. 3, respectively.

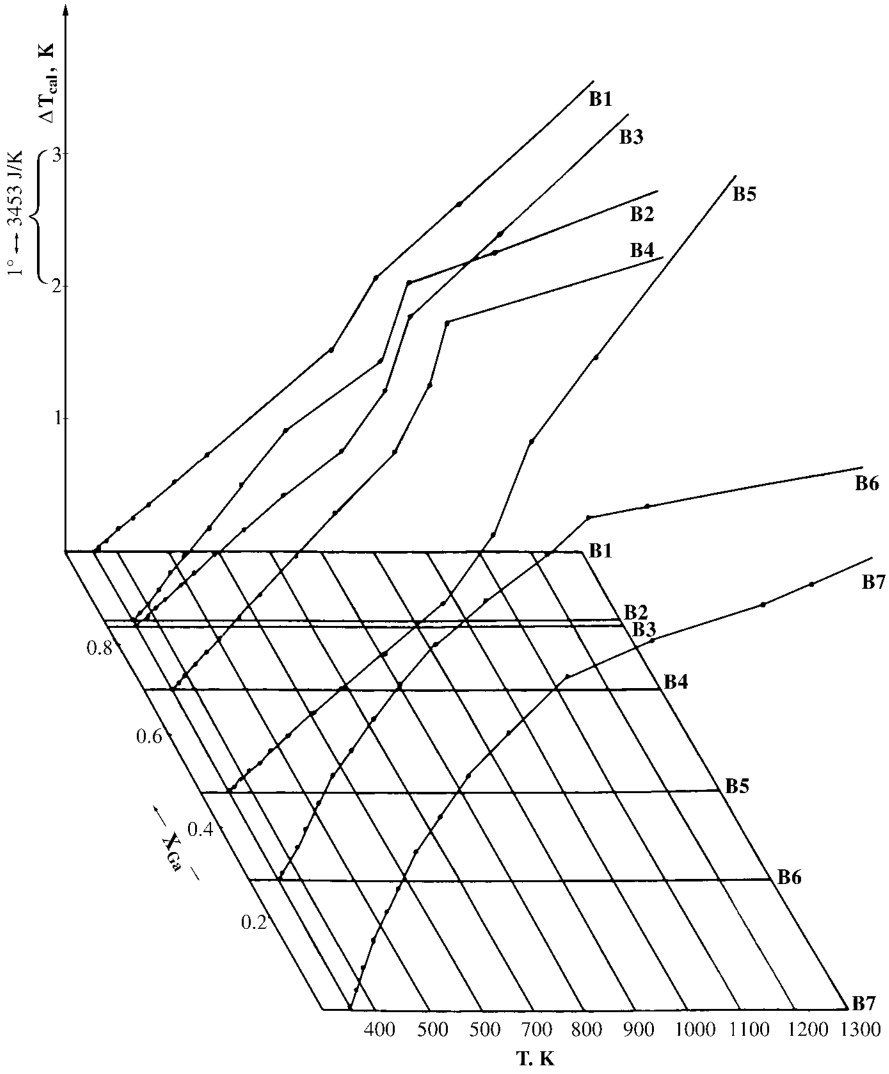

Fig. 3. The space diagram: the temperature change of the calorimetric vs. molar content and temperature for the binary system Ge–Sb.

Table 2
Results of the Oelsen quantitative thermodynamic analysis

SYSTEM Ge–Ga

No.	T (K)	a_{Ge}	a_{Ga}	γ_{Ge}	γ_{Ga}	$G^{xs}_{\mathrm{Ge}} = RT \ln \gamma_{\mathrm{Ge}}$ (J mol^{-1})	$G^{xs}_{\mathrm{Ga}} = RT \ln \gamma_{\mathrm{Ga}}$ (J mol^{-1})	$G^{M}_{\mathrm{Ge}} = RT \ln a_{\mathrm{Ge}}$ (J mol^{-1})	$G^{M}_{\mathrm{Ga}} = RT \ln a_{\mathrm{Ga}}$ (J mol^{-1})
A1	1073	0	1	–	1	–	0	–	0
A2		0.0001	0.9999	1	1	0	0	−82164.7	−0.89214
A3		0.123	0.786	0.635	0.975	−4051.26	−225.858	−18694.4	−2148.14
A4		0.289	0.532	0.74	0.872	−2686.14	−1221.86	−11073.8	−5630.1
A5		0.483	0.335	0.818	0.818	−1792.15	−1792.15	−6492.1	−9756.14
A6		0.718	0.139	0.905	0.673	−890.489	−3532.77	−2955.37	−17603.5
A7		1	0	1	–	0	–	0	–
A1	1173	0	1	–	1	–	0	–	0
A2		0.0001	0.9999	1	1	0	0	−89822.2	−0.97528
A3		0.131	0.805	0.677	0.998	−3804.22	−19.5242	−19822.2	−2115.41
A4		0.304	0.561	0.779	0.92	−2435.59	−813.164	−11612.4	−5637.18
A5		0.505	0.349	0.855	0.852	−1527.74	−1562.02	−6662.76	−10266.1
A6		0.731	0.147	0.921	0.712	−802.57	−3312.64	−3055.81	−18698.3
A7		1	0	1	–	0	–	0	–
A1	1273	0	1	–	1	–	0	–	0
A2		0.0001	0.9999	1	1	0	0	−97479.7	−1.05848
A3		0.142	0.815	0.733	1.011	−3287.41	115.7853	−20658.7	−2165.19
A4		0.327	0.589	0.838	0.966	−1870.54	−366.106	−11830.4	−5602.54
A5		0.533	0.36	0.903	0.879	−1079.89	−1364.99	−6659.64	−10813.4
A6		0.768	0.154	0.968	0.745	−344.216	−3115.54	−2793.74	−19801
A7		1	0	1	–	0	–	0	–

SYSTEM Ge–Sb

No.	T (K)	a_{Ge}	a_{Sb}	γ_{Ge}	γ_{Sb}	$G^{xs}_{\mathrm{Ge}} = RT \ln \gamma_{\mathrm{Ge}}$ (J mol^{-1})	$G^{xs}_{\mathrm{Sb}} = RT \ln \gamma_{\mathrm{Sb}}$ (J mol^{-1})	$G^{M}_{\mathrm{Ge}} = RT \ln a_{\mathrm{Ge}}$ (J mol^{-1})	$G^{M}_{\mathrm{Sb}} = RT \ln a_{\mathrm{Sb}}$ (J mol^{-1})
B1	1073	0	1	–	1	–	0	–	0
B2		0.204	0.908	1.405	1.062	3033.446	536.6285	−14181	−860.966
B3		0.212	0.903	1.349	1.071	2670.599	611.9109	−13837.9	−910.226
B4		0.351	0.772	1.188	1.096	1536.818	817.7558	−9339.93	−2308.47
B5		0.572	0.551	1.084	1.167	719.5429	1377.715	−4983.37	−5317.05
B6		0.758	0.351	1.059	1.234	511.3924	1875.721	−2471.74	−9339.93
B7		1	0	1	–	0	–	0	–
B1	1173	0	1	–	1	–	0	–	0
B2		0.2	0.892	1.377	1.044	3119.838	419.93	−15695.8	−1114.58
B3		0.206	0.887	1.311	1.052	2640.833	494.3756	−15407.5	−1169.4
B4		0.343	0.758	1.161	1.076	1455.843	714.3621	−10435.2	−2702.09
B5		0.561	0.535	1.063	1.133	595.8191	1217.763	−5637.18	−6099.97
B6		0.74	0.343	1.034	1.206	326.0667	1826.699	−2936.47	−10435.2
B7		1	0	1	–	0	–	0	–
B1	1273	0	1	–	1	–	0	–	0
B2		0.194	0.861	1.336	1.007	3065.893	73.82796	−17356.2	−1583.97
B3		0.2	0.856	1.273	1.016	2554.66	167.9991	−17033.8	−1645.61
B4		0.333	0.735	1.127	1.043	1265.382	445.5871	−11638	−3258.57
B5		0.551	0.519	1.044	1.099	455.7297	999.1105	−6308.11	−6941.35
B6		0.719	0.333	1.005	1.171	52.78675	1670.726	−3491.51	−11638
B7		1	0	1	–	0	–	0	–

According to the Oelsen thermodynamic analysis [11], the next step is graphic planimetry, which enables further quantitative thermodynamic analysis.

The construction of the tangent for the determination of $-R\ln a_{\mathrm{Ge}}$ and $-R\ln a_{\mathrm{Ga}}$ at 1273 K is shown in Fig. 4, and for the determination of $-R\ln a_{\mathrm{Ge}}$ and $-R\ln a_{\mathrm{Sb}}$ at 1273 K in Fig. 5.

The results of the Oelsen quantitative thermodynamic analysis, which include values for activities, activity coefficients, partial molar Gibbs energy of mixing and partial molar Gibbs excess energy for germanium, gallium and antimony in the range 1073–1273 K, for investigated systems, are given in Table 2.

The dependence of the activity of germanium and gallium on the molar content at 1073, 1173 and 1273 K is presented in Fig. 6, and the dependence of the activity of germanium and antimony on the molar content at 1073, 1173 and 1273 K is presented in Fig. 7. The obtained results for activity at 1273 K show good agreement with ref. [6,9].

A negative deviation from Raoult's law is noticed for binary system Ge–Ga, except for values of molar content from $x_{\mathrm{Ga}} = 0$ to $x_{\mathrm{Ga}} = 0.25$ at temperature of 1273 K where a positive deviation from Raoult's law is noticed. This indicates good miscibility between the components, especially at higher temperatures, whereas gallium is not practically good mixing with germanium at 1273 K from $x_{\mathrm{Ga}} = 0$ to 0.25. Also, it is noticed that activity coefficients for gallium and germanium are less than unity in all compositional range of investigated system Ge–Ga. With increasing molar content of germanium and gallium, the activity coefficients increase uniformly at all investigated temperatures, and point to fact that deviation from Raoult's

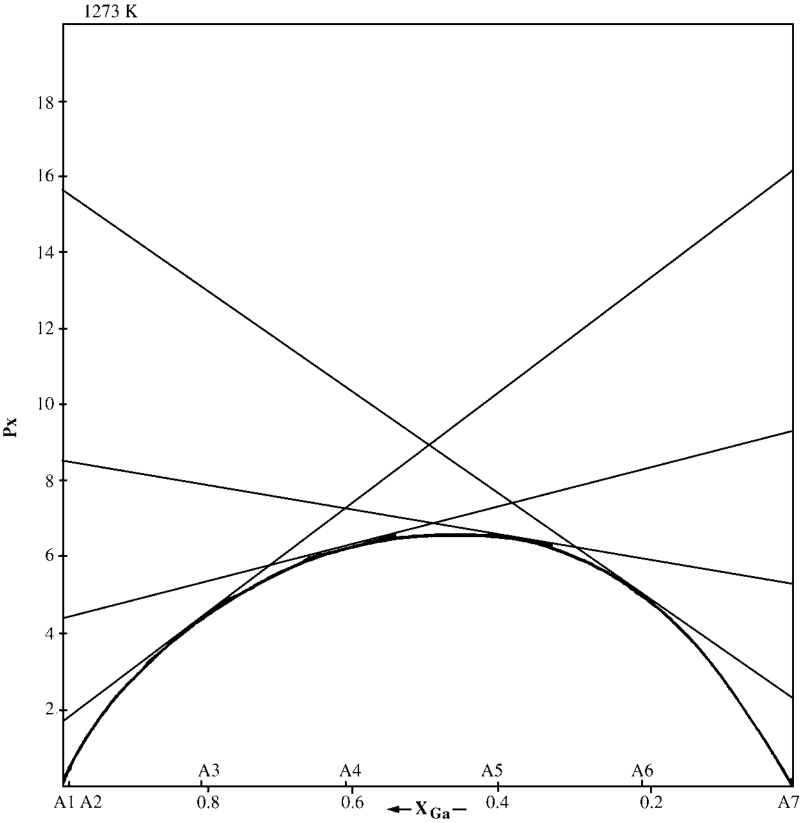

Fig. 4. The construction of the tangent for determination of $-\mathrm{Rlna_{Ge}}$ and $-\mathrm{Rlna_{Ga}}$.

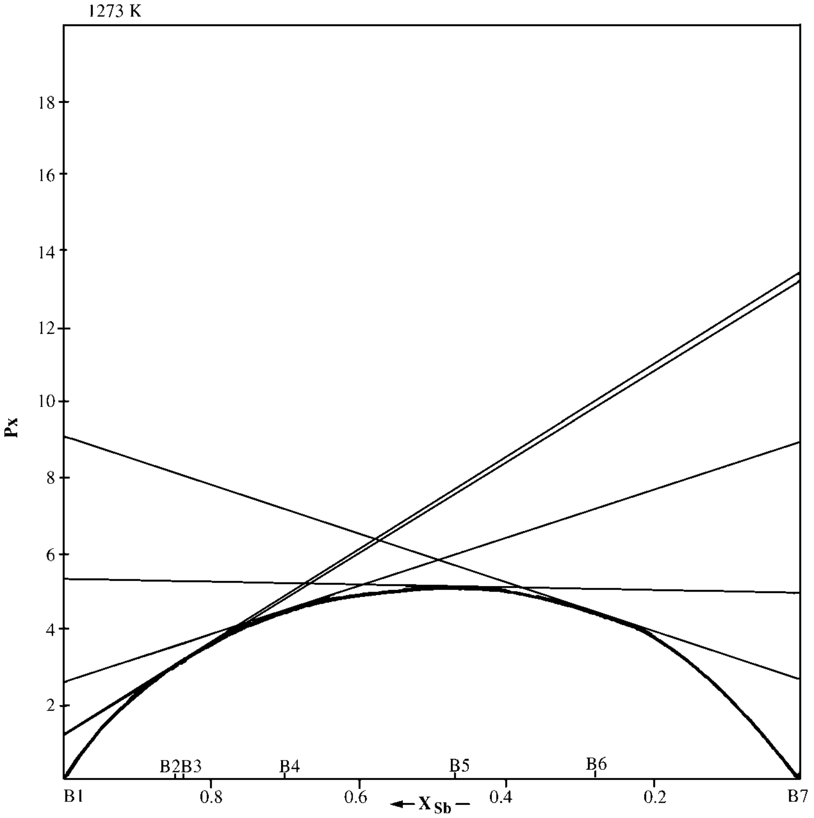

Fig. 5. The construction of the tangent for determination of $-R\ln a_{Ge}$ and $-R\ln a_{Sb}$.

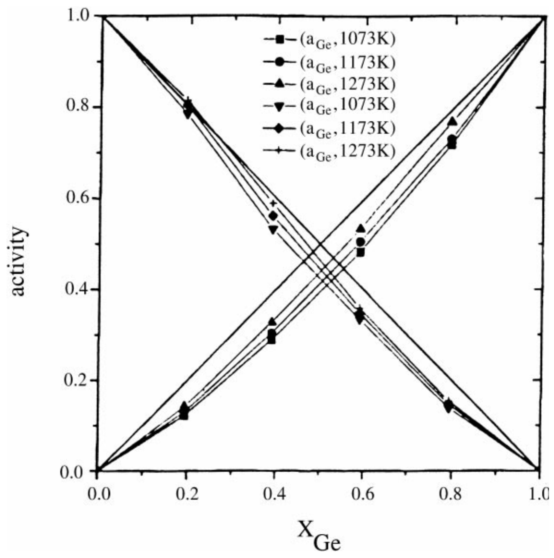

Fig. 6. Activity of Ge and Ga vs. molar content at 1073, 1173 and 1273 K.

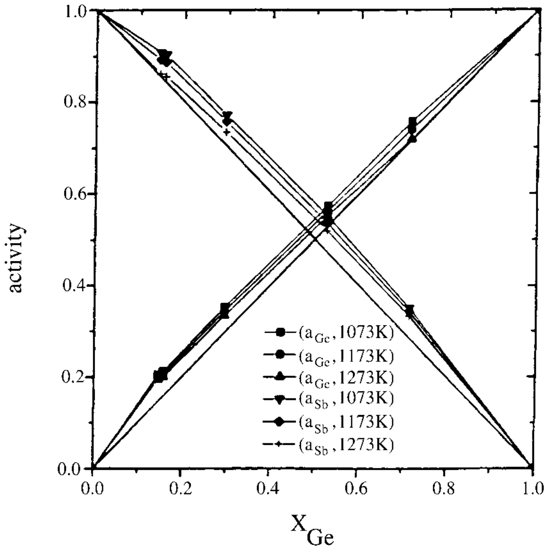

Fig. 7. Activity of Ge and Sb vs. molar content at 1073, 1173 and 1273 K.

law is less at higher temperatures. In the same way, with increasing temperature for all investigated compositions, the activity coefficients increase uniformly. Obtained values of the partial excess Gibbs energies for germanium and gallium confirm the conclusions about the thermodynamic behavior of binary system Ge–Ga with respect to Raoult's law. The dependence of the partial Gibbs energy of mixing for germanium and gallium on the molar content and temperature show increasing. Namely, with increasing molar content and temperature, the negativity of that function increases.

Similarly, for the investigated binary system Ge–Sb, a positive deviation from Raoult's law is noticed in all compositional range. The activity coefficients are larger than unity and decrease uniformly with increasing molar content of germanium and antimony at all investigated temperatures, and point to fact that deviation from Raoult's law is larger at higher temperatures. Also, the obtained values for partial excess Gibbs energies and partial Gibbs energy of mixing for germanium and antimony confirm the conclusions about the thermodynamic behavior of this system with respect to Raoult's law.

The obtained thermodynamic data for the investigated binary systems Ge–Ga and Ge–Sb describe those systems completely thermodynamically at temperatures of 1073, 1173 and 1273 K. In the same way those thermodynamic data present the starting base for all further investigations, connected with multi-component systems in which these binary systems are included.

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References

[1] L.H. Belz, Adv. Mater. Process. Inc. Met. Prog. 132(5) (1987) 65–69.
[2] M.C. Roberts, Materials and Society 13(4) (1989) 411–430.
[3] I. Ansara, J.P. Bros, M. Gambino, CALPHAD 3(3) (1979) 225–233.
[4] H. Eslami, Y.M. Muggianu, M. Gambino, J.P. Bros, P. Leydet, J. Less-Common Metals 64 (1979) 31–44.
[5] H. Eslami, J. Franceschi, M. Gambino, J.P. Bros, Z. Naturforsch., 34 (a) (1979) 810–817.
[6] M. Fornaris, Y.M. Muggianu, M. Gambino, J.P. Bros, Z. Naturforsch., 35 (a) (1980) 1256–1264.
[7] J. Franceschi, M. Fornaris, M. Gambino, J.P. Bros, Canadian Metallurgical Quarterly 21(3) (1982) 273–279.
[8] J. Šestak, V. Šestakova, Ž. Živković, D. Živković, Pure Appl. Chem. 67(11) (1995) 1885–1890.
[9] B. Predel, D.W. Stein, Z. Metallkd. 61(12) (1970) 909–914.
[10] P.Y. Chevalier, Thermochimica Acta 155 (1989) 227–240.
[11] W. Oelsen, Arch. Eisenhnettenwes 26 (1955) 519–522.
[12] D. Živković, Ž. Živković, J. Šestak, Thermochimica Acta 230 (1993) 65–75.
[13] D. Živković, Ž. Živković, J. Šestak, J. Therm. Analysis 52 (1998) 393–401.
[14] R.W. Olesinski, G.J. Abbaschian, Binary Alloys Phase Diagrams 6(3) (1985) 258–262.
[15] R.W. Olesinski, G.J. Abbaschian, Binary Alloys Phase Diagrams 7(3) (1986) 219–222.