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CALORIMETRIC INVESTIGATION OF LIQUID Ga-Me (Me = Sn, Zn) ALLOYS USING OELSEN METHOD

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The results of calorimetric investigation of binary, liquid Ga-Me (Sn, Zn) alloys are presented in this paper. According to constructed space enthalpy diagram and enthalpy isotherm diagram, activities, activity coefficients and other partial and integral molar quantities were determined at different temperatures. Also, comparison was made with existing literature data.

Key words: *thermodynamics, calorimetric, gallium alloys, Ga-Sn, Ga-Zn*

Kalorimetrijsko ispitivanje tekućih Ga-Me (Sn, Zn) legura Oelsenovom metodom. U radu su prikazani rezultati kalorimetrijskog ispitivanja tekućih Ga-Me (Sn, Zn) legura po Oelsenovoj metodi. Na temelju određenog prostornog dijagrama entalpija, kao i dijagrama entalpijskih izotermi, proračunate su vrijednosti aktivnosti, koeficijenata aktivnosti i parcijalnih molarnih veličina komponenti na različitim temperaturama. Dobiveni rezultati su uspoređeni s literaturnim podacima.

Ključne riječi: *termodinamika, kalorimetrija, legure galija, Ga-Sn, Ga-Zn*

INTRODUCTION

Gallium-based alloys are mostly known for their low melting eutectics, caused by existence of gallium. Two eutectic systems, Ga-Sn and Ga-Zn (Figure 1.), belong to this group and present the constituents of different gallium-based multicomponent alloys applied in industry of semiconducting materials.

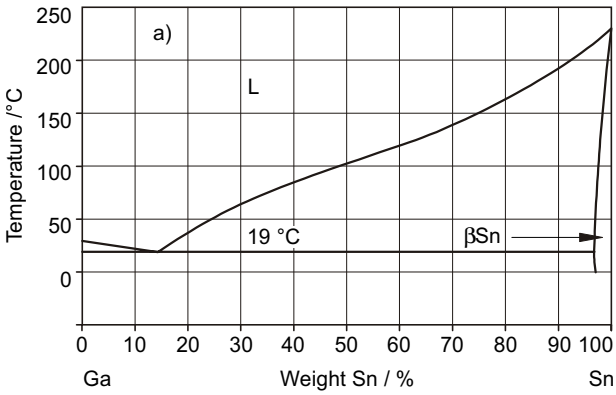

Figure 1. **Phase diagrams of binary systems: a) Ga-Sn and b) Ga-Zn**
Slika 1. **Fazni dijagrami binarnog sustava: a) Ga-Sn i b) Ga-Zn**

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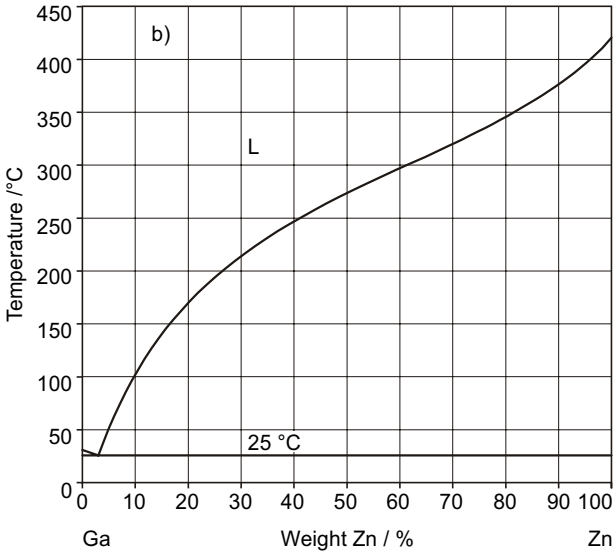
There are a lot of references in literature on thermodynamic properties of mentioned binary gallium-based systems. Many researchers worked on Ga-Sn thermodynamics [3 - 10]. Cohen et al. [3] determined the heat of solution of Ga in liquid Sn. Predel [4] explored this system by several experimental methods and calculated values of ΔG^M and ΔS^M for liquid alloys. Pool and Lundin [5] did tin solution calorimetry measurements, while Danilin and Yatsenko



[6] performed EMF measurements. Bros and Laffite [7] determined the enthalpy of formation of the liquid alloys at temperatures 400-750 K in the whole concentration range using microcalorimetry. Hultgren and coworkers presented the compilation of data published up to 1973 in their well known book [8], while Muggianu et al. [9] determined mixing enthalpies for Ga-Sn alloys. Most recent works on Ga-Sn thermodynamics are EMF measurements with zirconia solid electrolyte done by Katayama et al. [10] and quantitative DTA measurements performed by Živković et al. [11].

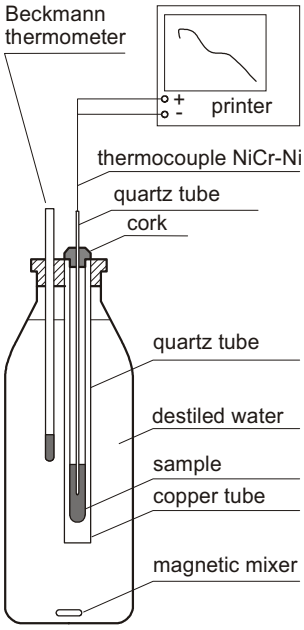


Figure 2. **Graphical representation of used Oelsen calorimeter**
Slika 2. **Grafički prikaz korištenog Oelsenovog kalorimetra**

Thermodynamics of Ga-Zn system has been investigated by several different experimental methods. There are many results obtained using EMF measurements by: Genta et al. [12], Svirbley and Read [13], Gerasimenko et al. [14], Predel et al. [15], Ryabov and Sryvalin [16] and Moser [17]. Vapor pressure measurements were performed by Piacente et al. [18], calorimetric measurements were done by Kleppa [19], while results of quantitative DTA measurements were presented recently by Živković et al. [11] Also, there are some results obtained using thermodynamic calculations by Lukas et al. [20] and Hajra and Mazumdar [21]. Complete thermodynamic data on Ga-Zn system are presented in [8] and in the work of Dutkiewicz et al. [22].

Results of thermodynamic analysis of liquid binary Ga-Sn and Ga-Zn alloys, according to Olesen calorimetry, are presented in this paper and compared with literature data.

EXPERIMENTAL

Oelsen calorimetry was applied for thermodynamic investigation of Ga-Sn and Ga-Zn systems [23 - 25]. The main experimental procedure according to Oelsen calorimetry is performed as follows: sample alloys are heated in electro-resistive furnace to a temperature above liquidus line, and then quickly put into Oelsen's calorimeter (Figure 2.) in which temperature change of calorimeter and temperature of a sample are measured as a function of time using Beckmann thermometer and NiCr-Ni thermocouple,

Table 1. **Composition and masses of the investigated Ga-Sn and Ga-Zn alloys**
Tablica 1. **Sastavi i mase ispitivanih Ga-Sn i Ga-Zn legura**

Ga - Sn			Ga - Zn		
Sample	*x*Ga	Mass / g	Sample	*x*Ga	Mass / g
L1	1,0	2,9550	S1	1	1,7730
L2	0,95	3,0021	S2	0,9628	1,7838
L3	0,9258	3,0241	S3	0,8616	1,8139
L4	0,8	3,1332	S4	0,5890	1,9027
L5	0,6	3,2878	S5	0,3054	2,0086
L6	0,3	3,4852	S6	0,1978	2,0530
L7	0,0	3,6500	S7	0	2,1420

respectively, and recorded by printer. Full description of this experimental technique and its theoretical fundamentals is reported in [23 - 25].

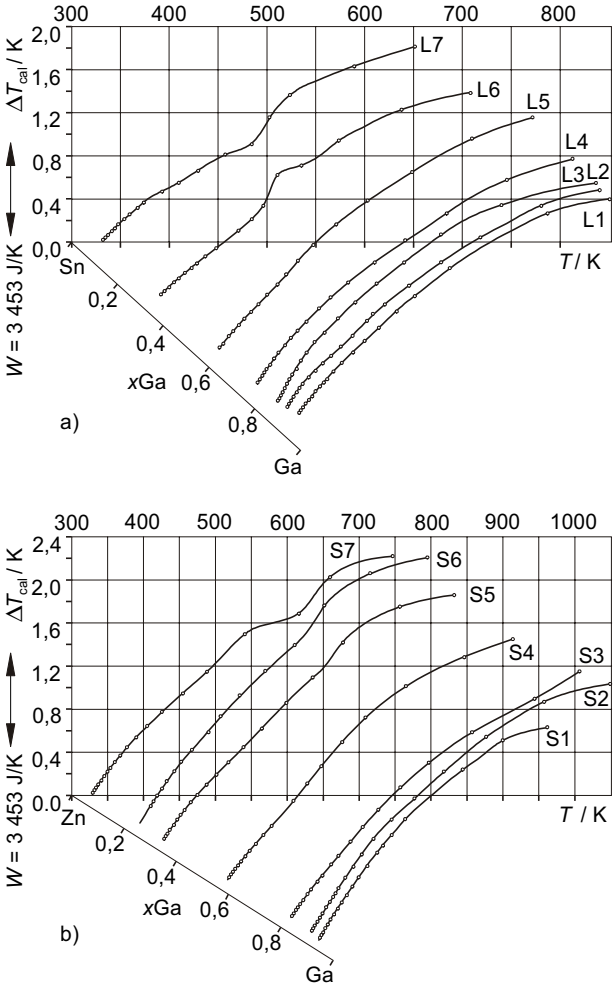


Figure 3. **Space enthalpy diagram: a) Ga-Sn system and b) Ga-Zn system**
Slika 3. **Prostorni dijagram entalpije: a) Ga-Sn sustav i b) Ga-Zn sustav**

Metals (Ga, Sn and Zn) used in this work were of p.a. purity. The compositions of the investigated alloys in Ga-Sn and Ga-Zn systems are given in Table 1. According to the requirements of the method used, volume of samples was constant 0,5 cm^3 and 0,3 cm^3 for Ga-Sn and Ga-Zn system, respectively.

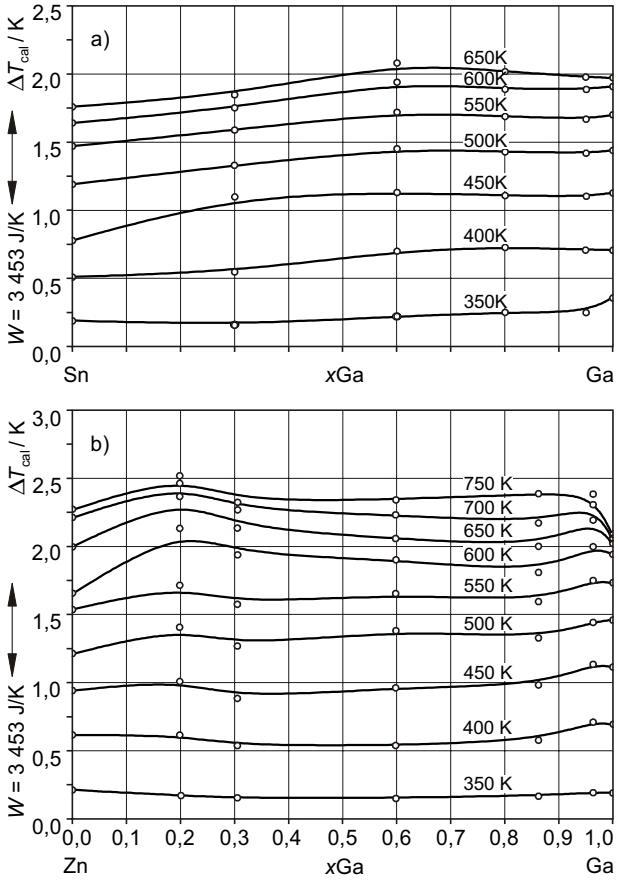


Figure 4. **Enthalpy isotherm diagram: a) Ga-Sn system and b) Ga-Zn system**
Slika 4. **Dijagram entalpijskih izotermi: a) Ga-Sn sustav i b) Ga-Zn sustav**

The water equivalent was determined by a standard method using dissolved Na_2CO_3 and for the calorimeter used it was found to be 3453 J/K. Calibration of used NiCr-Ni thermocouple was done using pure metals Ga, Sn, Bi, Pb and Zn.

RESULTS AND DISCUSSION

Based on obtained cooling curves temperature change of calorimeter (ΔT cal) was determined for all samples investigated in temperature range 350 to 650 K (for Ga-Sn alloys) and 350 to 750 K (for Ga-Zn alloys), which enabled construction of space enthalpy diagrams and enthalpy isotherm diagrams. These diagrams are given in Figures 3. - 4. for Ga-Sn and Ga-Zn system, respectively.

Comparison between values for the integral molar enthalpies of mixing obtained for Ga-Sn and Ga-Zn alloys by Oelsen calorimetry and literature data [7, 8, 11] and [8, 11, 22], respectively, is presented graphically in Figure 5.

As can be seen from Figure 5., low positive values for ΔH^M are noticed in the case of both systems. Ga-Sn alloys have maximum value of integral molar enthalpies of mixing equal to 0,75 kJ/mol, while Ga-Zn alloys posses a little bit higher maximum of 1,4 kJ/mol. There is a slight deviation between results of Oelsen calorimetry and literature, and in both cases results of this work are somehow lower. But, since enthalpy values are of very small magnitude (less then 1,5 kJ/mol), such error should not have extremely significant importance [11].

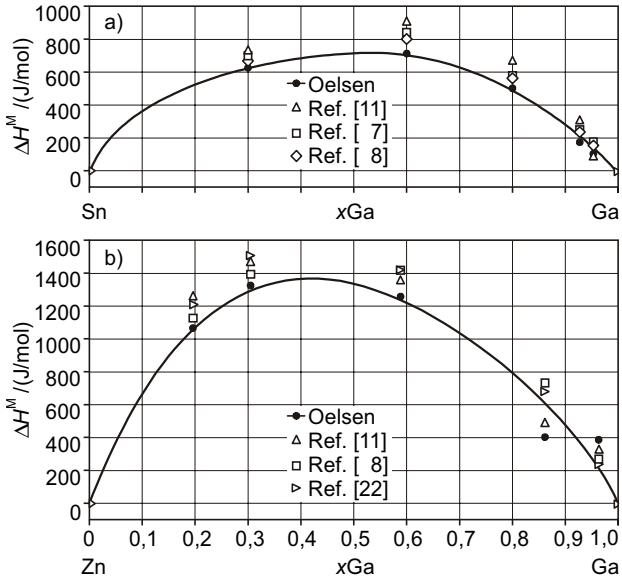


Figure 5. **Comparative review of ΔH^M values obtained by Oelsen calorimetry and literature: a) Ga-Sn system and b) Ga-Zn system**
Slika 5. **Usporedni pregled vrijednosti ΔH^M dobivenih Oelsenovom kalorimetrijom i literaturom: a) Ga-Sn sustav i b) Ga-Zn sustav**

Having in mind these low heat effects, typical for Ga-Sn and Ga-Zn systems, further calculation of other partial and integral molar thermodynamic quantities was done based on Gibbs-Helmholtz equation:

$$\Delta G^M = \Delta H^M - T\,\Delta S^M_{id} \quad (1)$$

where ΔG^M is integral molar Gibbs energy of mixing and ΔS^M_{id} is ideal integral molar entropy of mixing:

$$\Delta S^M_{id} = -R\,\Sigma x_i \ln x_i \quad (2)$$

Partial molar Gibbs energies of mixing were determined by fitting ΔG^M vs. composition and according to relation:

$$G^{M}_{i} = \Delta G^{M} + (1 - x_i)\times(\partial \Delta G^{M}/\partial x_i) \quad (3)$$

where G^{M}_{i} presents partial molar Gibbs energy of mixing. Results obtained by given calculation procedure, at the temperatures of 600 and 650 K for Ga-Sn system and at the temperature of 723 K for Ga-Zn system, are presented in Table 2., including activities, activity coefficients and other partial and integral molar quantities. Positive deviation from Raoult law can be noticed for both investigated systems indicating to a low mutual attraction between components, stronger expressed in the case of Ga-Zn alloys, while Ga-Sn alloys show moderately positive deviations from ideal solution behavior.

Comparison was made with literature, for both systems: activities for gallium and tin in Ga-Sn system, obtained by Oelsen calorimetry, were compared with [4] while activities for gallium and zinc in Ga-Zn system, obtained by Oelsen calorimetry, were compared with [8, 11].

Comparative review (Figure 6.) points out to a slight deviation between Oelsen calorimetry results and literature, while better agreement is noticed for Ga-Sn system. This can be explained by lower heat effect of mixing presented in this binary system. It means that these alloys are closer to regular behavior and applied calculation procedure including ideal integral molar entropy of mixing gives more accurate results. Also, one may perceive for Ga-Zn system (Figure 6.b) that there exist better agreement between results of this work and [11] comparing to [8]. Reason for that could be similar calculation procedure applying regular model, which was used in [11], too.

Table 2. **Partial and integral molar quantities obtained by Oelsen calorimetry: a) Ga-Sn system, b) Ga-Zn system**
Tablica 2. **Parcijalne i integralne molarne veličine dobivene Oelsenovom kalorimetrijom: a) Ga-Sn sustav, b) Ga-Zn sustav**

a) T = 600 K

xGa	ΔH^{M}	ΔS^{M}_{id}	ΔG^{M}	G^{m}_{Ga}	aGa	γGa	G^{xs}_{Ga}	G^{M}_{Sn}	a*S*n	γ*S*n	G^{xs}_{Sn}
1	0	0	0	0	1	1	0		0		
0,95	104	1,650	–886	–406	0,922	0,970	–150	–10008	0,134	2,689	4936
0,9258	180	2,198	–1139	–466	0,911	0,984	–81	–9539	0,148	1,991	3436
0,8	511	4,160	–1985	–721	0,865	1,082	392	–7043	0,244	1,218	985
0,6	732	5,595	–2625	–1846	0,691	1,151	703	–3795	0,467	1,168	776
0,3	625	5,079	–2422	–5650	0,322	1,074	356	–1039	0,812	1,159	740
0	0	0	0		0			0	1	1	0

T = 650 K

xGa	ΔH^{M}	ΔS^{M}_{id}	ΔG^{M}	G^{m}_{Ga}	aGa	γGa	G^{xs}_{Ga}	G^{M}_{Sn}	a*S*n	γ*S*n	G^{xs}_{Sn}
1	0	0	0	0	1	1	0	0	0		
0,95	104	1,650	–969	–489	0,907	0,954	–233	–10091	0,132	2,646	4853
0,9258	180	2,198	–1249	–575	0,891	0,962	–191	–9649	0,145	1,948	3326
0,8	511	4,160	–2193	–929	0,830	1,038	184	–7251	0,234	1,169	777
0,6	732	5,595	–2905	–2125	0,653	1,088	423	–4074	0,442	1,105	496
0,3	625	5,079	–2676	–5904	0,306	1,021	102	–1293	0,772	1,102	486
0	0	0	0		0			0	1	1	0

b) T = 723 K

xGa	ΔH^{M}	ΔS^{M}_{id}	ΔG^{M}	G^{m}_{Ga}	aGa	γGa	G^{xs}_{Ga}	G^{M}_{Sn}	aZn	γZn	G^{xs}_{Zn}
1	0	0	0	0	1	1	0		0		
0,9628	398	1,321	–395	–102	0,983	1,021	126	–7977	0,265	7,131	11808
0,8616	414	3,343	–1592	–747	0,883	1,025	149	–6850	0,319	2,312	5037
0,5890	1268	5,630	–2110	–1563	0,771	1,309	1619	–2894	0,618	1,503	2451
0,3054	1325	5,116	–1745	–4269	0,491	1,609	2861	–635	0,899	1,295	1566
0,1978	1067	4,135	–1414	–5840	0,378	1,913	3901	–323	0,948	1,181	1002
0	0	0	0		1			0	1	1	0

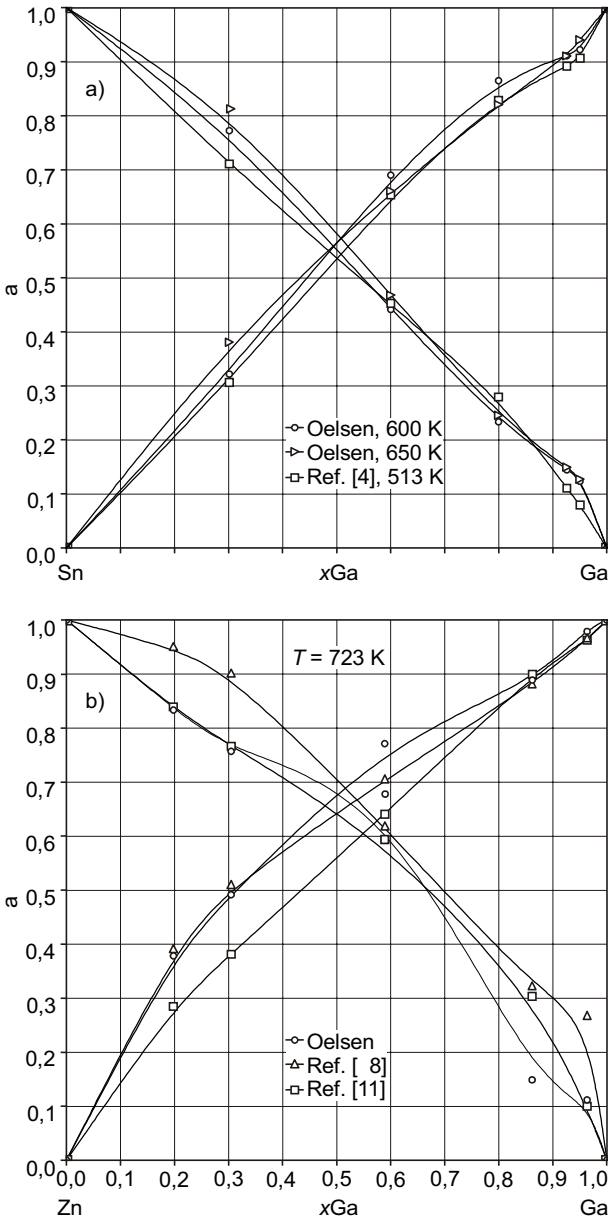


Figure 6. **Comparison between thermodynamic data obtained by Oelsen calorimetry and literature: a) Ga-Sn system and b Ga-Zn system**

Slika 6. **Usporedba termodinamičkih parametara dobivenih Oelsenovom kalorimetrijom i literature: a) Ga-Sn sustav i b) Ga-Zn sustav**

CONCLUSIONS

Results of Olesen calorimetry application to liquid gallium-based binary Ga-Sn and Ga-Zn alloys are presented in this paper. Space enthalpy diagrams and enthalpy isotherm diagrams were constructed based on cooling curves obtained in Oelsen calorimeter, and integral molar enthalpies of mixing in liquid state were determined. In further calculation procedure, other partial and integral molar quantities (for Ga-Sn system at 600 - 650 K and for Ga-Zn system at 723 K) were obtained. Comparison of results obtained by this method and literature data show reasonable agreement in both cases.

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