THERMODYNAMIC CALCULATION OF THE BINARY SYSTEMS Bi-Sn BY IMPLEMENTING A JAVA INTERFACE

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The paper presents the results of the thermodynamic activity quantities, the activity coefficient quantities as well as the excess partially molar free-energy and partially molar free-energy of mixing quantities. The thermodynamic activities of the Bi-Sn system at temperature of 600K were measured in a reversible concentration cell by means of the electromotive voltage (mV) determinations. The electrolyte consisted in a mixture of stannic chloride and potassium chloride salts (17% moles KCl and 83% moles SnCl2). The measurements were performed on the concentration range $\chi Bi \in (0.1)$ with a step of the atomic fraction of 0.1. The melting temperature of the electrolyte was 563.15K (290^0C). For the purpose of thermodynamic characterization of the Bi-Sn alloy, was calculated and graphically represented the thermodynamic quantities using the software entitled "Thermodynamic calculations for binary systems - TCBS" design by the authors, which was developed using the NetBeans IDE 8.0.2 in Java programming language and allows the calculation and analysis of the thermodynamic activities of Bi, Sn as well as the comparison of the results obtained with the existing data in the specialized literature.

Keywords: Bi-Sn alloys; activity coefficient; thermodynamic modeling; Java interface

1. Introduction

The data regarding the thermodynamic activities of some binary alloys for different temperatures are found in the specialized literature, but most were obtained between the years 1915-1970. During this time, the outdated working methodology and inaccurate calculation methods made us ask ourselves a question about the accuracy of the already existing results. It was found necessary

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a software whereby, by introducing the data obtained in the laboratory it will calculate automatically the thermodynamic activities with greater precision.

Analyzing the specialized works in this field we have found that Bi-Sn binary alloys are used very often in electrotechnics and electronics. These types of alloys require a set of physical-chemical characteristics suitable for different applications, but little thermodynamic data related to certain working temperatures are known. Thus, the study of the various processes in thermodynamics requires the knowledge of the mechanism of the phenomena that lead to the respective processes [1, 2, 3, 4].

In the thermodynamics are established relationships between quantities directly observable, between measurable quantities in macroscopic experiments. The determination of the thermodynamic activity based on the measurement of the electromotive voltage relies on the measurement of the electromotive voltage in a reversible concentration cell using solid or liquid electrolyte [5, 6, 7]. The electrochemical systems in which the electrodes differ only by the activity (concentration) of the components are called concentration cells. In a cell of this type the energy source is represented by the transfer energy from the higher activity substance to the lower activity substance.

The dependence of the thermodynamic properties on the state parameters cannot be determined theoretically, with sufficient precision, therefore resorting often formal description of these properties based on empirical relationships. This way of treating the problem proves to be useful in the practical solution of some problems of elaboration of the alloys or of thermal refining of the metals when the emphasis is mainly on the agreement between the model and the experimental data and less on the connection between the model and the interactions between elementary particles [8, 9, 10, 11, 12].

As early as 1895 Margules [13] proposed the use of calculations of Gibbs free-energies integral-molar and partially-molar of excess. Most mixtures deviate from ideal behavior. Most thermodynamic quantities are relative; they refer to a reference state. The main standard states used are based on Raoult's law [14, 15].

According to Raoult's law, the fugacity and therefore the activity is proportional to the molar fraction x. For the thermodynamic characterization of the Bi-Sn alloy, was calculated and graphically represented the thermodynamic activity quantities, the activity coefficient quantities as well as the partially molar excess free energy quantities (the difference between the functions of the real solutions and the functions corresponding to the ideal solutions). These sizes characterize the deviation from ideal mixing state. For this purpose, was used the software entitled "*Thermodynamic calculations for binary systems - TCBS*" design by the authors, which was developed using the NetBeans IDE 8.0.2 in Java programming language. This software allows the calculation and analysis of the

thermodynamic activities of Bi, Sn as well as the comparison of the results obtained with the existing data in the specialized literature [16].

2. Materials and methods

The thermodynamic activities of the Bi-Sn system at temperature of 600K were measured in a reversible concentration cell by means of the electromotive voltage (mV) determinations. The electrolyte used in this work consisted in a mixture of stannic chloride - $SnCl_2$ and potassium chloride - KCl salts of 17% moles KCl and 83% moles $SnCl_2$. The $SnCl_2$ and KCl salts of analytical purity were purchased from Silver Chemicals. The measurements were performed on the concentration range $\chi_{Bi} \in (0.1)$ with a step of the atomic fraction of 0.1.

The measuring electrode consisted in Bi-Sn alloy with various compositions. Pure Bi was the reference electrode. The melting temperature of the electrolyte is 563.15K (290^0C). Tungsten (W) wires covered by quartz sheaths were put into contact with the melted electrodes of the cell because W is insoluble in Bismuth or in Bi-Sn alloy. Platinum wires were used to connect the W wires to the electronically measuring instrument.

During measurements, the cell was placed inside the furnace which is heated by a Kantal resistance. The furnace is equipped with a temperature control system that stabilized the temperature with a tolerance of 0.2^0C. The electrochemical system was maintained at constant temperature until the cell's electromotive voltage became constant, this being considered the equilibrium (*E*) electromotive voltage of the cell. The equilibrium value of the electromotive voltage was reached after about 20 minutes.

Within this work a Java interface for thermodynamic calculation of the binary systems Bi-Sn has been implemented. The software entitled "Thermodynamic calculations for binary systems - TCBS" realized in this article, was developed using the NetBeans IDE 8.0.2 in Java programming language [17]. This software allows the calculation and analysis of the thermodynamic activities of Bi, Sn as well as the comparison of the results obtained with the existing data in the specialized literature [18].

To be able to enter the data resulting from the experiments, the software can retrieve them from a file entitled *data.in*.

In the experiment, sets of 11 determinations were used for both Bi and Sn. Using in computing the form integrals $\int_a^b f(x)dx$ it was necessary to use functions that use notions of numerical calculation using Newton-Cotes methods [19, 20].

The method uses the Trapezoid rule and the Simpson's rule. The software created considers the solution by the two rules considering in case of unequal

results the result with the least calculation error. Thus Newton-Cotes methods start from the idea of approximating an integral defined in the form [19, 20]:

$$\int_x^y f(z) * w(z) * z(dz) = \sum_{i=0}^{N} A_{iN} * f(x_{iN}) + R_N \quad (1)$$

in which:
- $w(z) > 0$ represent the weight function,
- R_N - the error of the approximation formula.

In Newton Cotes' methods [19, 20] the abscissas are usually chosen equidistant in an interval [x, y] so that were determined the points:

$$z_{iN} = x + i * \frac{y-x}{N} \quad (2)$$

The error in Newton-Cotes methods is deduced by integrating the expression of the error in the interpolation polynomial, thus obtaining for N = 1 the trapezoid formula:

$$\int_x^y f(z)dz = \frac{h}{2} * [f(x) + f(y)] - \frac{h^3 * f''(\varepsilon)}{12} \quad (3)$$

where:
h = y – x
For N = 2 the Simpson's formula is obtained:

$$\int_x^y f(z)dz = \frac{h}{3} * \left[f(x) + 4 * f\left(\frac{y+x}{2}\right) + f(y)\right] - \frac{h^5 * f''(\varepsilon)}{90} \quad (4)$$

3. Experimental data

The electromotive voltage measuring method was used to estimate the $\Delta\bar{G}$, a and γ of the Bi and Sn into melted alloys with well-defined compositions. The software "Thermodynamic calculations for binary systems - TCBS" with the calculated data displays a window from which, with the help of thermodynamically relationship implemented in software routine, graphs with the analyzed data are obtained. The values of the electromotive voltage and the average of the values at the temperature of 600K were shown in Table 1.

Table 1

The average of the electromotive voltage's values at 600K

Temperature, K	**Electromotive voltages (mV)**									
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
Average	36.115	25.340	19.150	14.730	11.270	8.320	5.896	3.725	1.780	0.001

In Table 2 were rendered the experimental values of the thermodynamic activities for Bi at 600K compared with the ones from the specialized literature.

Experimental values were determined using the relationship of the implemented software and were graphically represented in Fig. 1.

Table 2

Thermodynamic activity of Bi at 600K

Molar fraction	1	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0.0
aBi - calculated	1	0.902	0.806	0.712	0.617	0.520	0.425	0.329	0.230	0.123	0.0
aBi - literature [13]	1	0.900	0.802	0.706	0.613	0.519	0.426	0.331	0.232	0.124	0.0

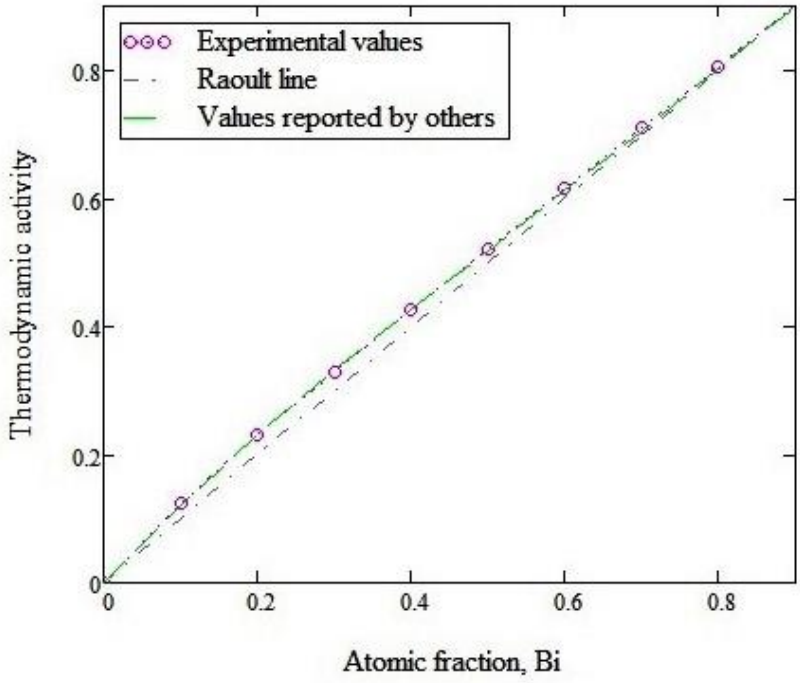

Fig. 1. Graphical representation of thermodynamic activity of Bi, using the software

In Table 3 were shown the experimental values of the thermodynamic activities for Sn at 600K calculated by using the implemented software and compared with the results from the specialized literature and were graphically represented in Fig. 2.

Table 3

Thermodynamic activity of Sn at 600K

Molar fraction	1	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0.0
aSn - calculated	1	0.903	0.806	0.715	0.620	0.525	0.428	0.329	0.225	0.116	0.0
aSn - literature [13]	1	0.904	0.813	0.723	0.632	0.537	0.439	0.337	0.229	0.116	0.0

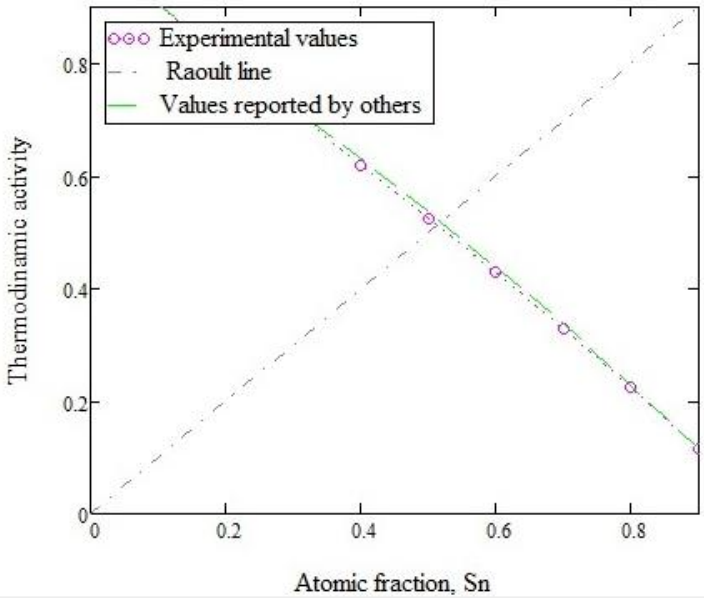

Fig. 2. Graphical representation of thermodynamic activity of Sn. Snapshot taken from the software used

In Tables 4 and 5 were indicated the values of the coefficients of the thermodynamic activities for Bi and Sn at 600K, experimental values calculated with the implemented software compared to the values in the specialized literature and were graphically represented in Fig. 3.

Table 4

Thermodynamic activity coefficients of Bi at 600K

Molar fraction	1	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0.0
ϒBi - calculated	1	1.002	1.008	1.017	1.030	1.051	1.076	1.121	1.174	1.253	1.310
ϒBi - literature [13]	1	1.000	1.002	1.009	1.021	1.039	1.065	1.104	1.160	1.241	1.356

Table 5

Thermodynamic activity coefficients of Sn at 600K

Molar fraction	1	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0.0
ϒSn - calculated	1	1.003	1.010	1.021	1.033	1.051	1.069	1.096	1.126	1.156	1.161
ϒSn - literature [13]	1	1.004	1.016	1.033	1.053	1.075	1.097	1.122	1.145	1.159	1.158

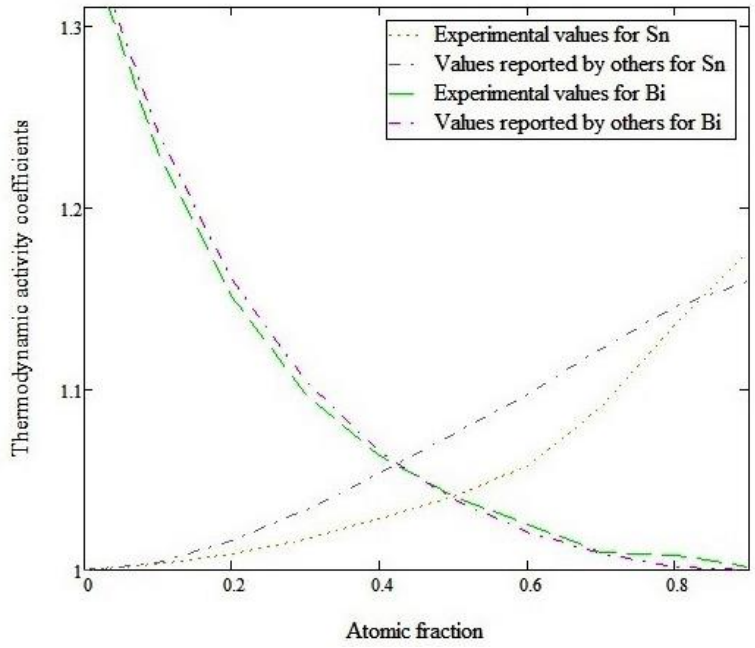

Fig. 3. Graphical representation of thermodynamic activity coefficients of Bi and Sn, using the software

In Tables 6 and 7 were shown the values of partially molar excess free energies for Bi and Sn, experimental values calculated with the implemented software compared with the values in the specialized literature and were graphically represented in Fig. 4.

Table 6

Partially molar excess free energies for Bi at 600K

Molar fraction	1	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0.0
$\Delta\bar{G}eBi$ *[J/mol] - calculated*	0	8.971	39.748	84.900	147.451	248.133	365.403	569.781	800.223	1125	+∞
$\Delta\bar{G}eBi$*[J/mol] -literature [13]*	0	9.967	44.695	103.672	190.850	314.143	493.552	740.378	1077	1519	+∞

Table 7

Partially molar excess free energies for Sn at 600K

Molar fraction	1	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0
$\Delta\bar{G}eSn$*[J/mol] - calculated*	0	14.943	49.636	103.672	161.959	248.133	332.844	457.273	591.980	723.174	+∞
$\Delta\bar{G}eSn$*[J/mol] - literature [13]*	0	19.914	79.183	161.959	257.617	360.764	461.822	574.229	675.450	731.77	+∞

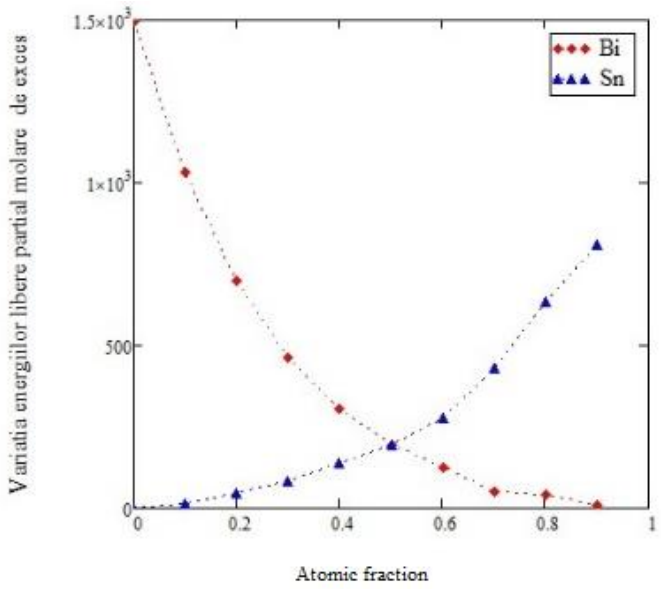

Fig. 4. Graphical representation of partially molar excess free energies for Bi and Sn. Snapshot taken from the software used

In Tables 8 and 9 were shown the values of partially molar free energies for Bi and Sn, experimental values calculated with the implemented software compared with the values in the specialized literature and were graphically represented in Fig. 5.

Table 8

Partially molar free energies of mixing for Bi at 600K

Molar fraction	1	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0.0
$\Delta\bar{G}Bi$ *[J/mol]] - calculated*	0	-547.80	-1070	-1667	-2370	-3186	-4210	-5396	-7224	-10370	-∞
$\Delta\bar{G}Bi$ *[J/mol] -literature [13]*	0	-525.58	-1101	-1737	-2441	-3272	-4257	-5515	-7288	-10580	-∞

Table 9

Partially molar free energies of mixing for Sn at 600K

Molar fraction	1	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0
$\Delta\bar{G}Sn$*[J/mol] - calculated*	0	-508.980	-1063	-1673	-2385	-3214	-4233	-5546	-7441	-10750	-∞
$\Delta\bar{G}Sn$*[J/mol] - literature [13]*	0	-503.459	-1033	-1618	-2289	-3102	-4107	-5426	-7353	-10750	-∞

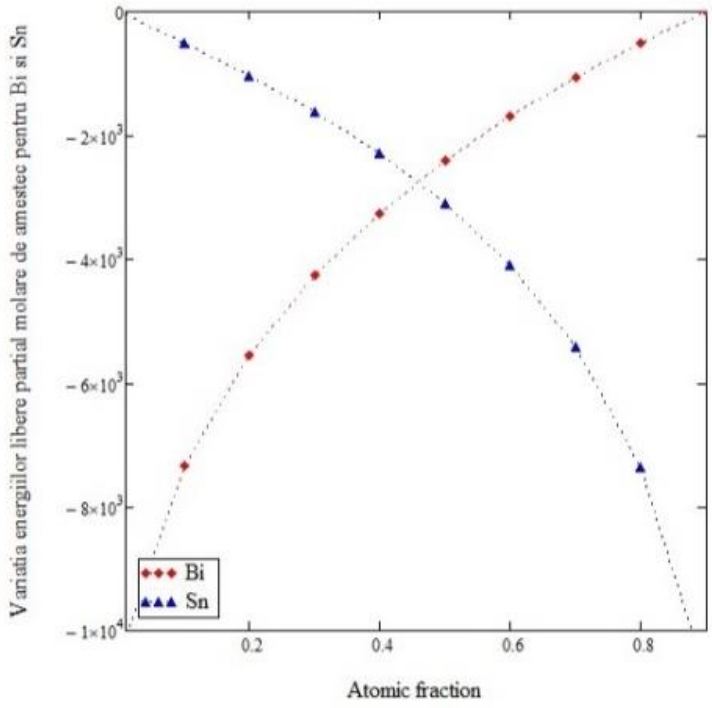

Fig. 5. Graphical representation of partially molar free energies of mixing for Bi and Sn. Snapshot taken from the software used

3. Conclusions

The electromotive voltage measuring method was used to estimate the $\Delta\bar{G}$, *a* and γ of the Bi and Sn into melted alloys with well-defined compositions. Were measured the thermodynamic activities of the Bi-Sn system at temperature of 600K means of the electromotive voltage (mV) determinations.

The electrochemical system was maintained at constant temperature until the cell's electromotive voltage became constant (considered the equilibrium (*E*) electromotive voltage of the cell). The thermodynamic data were achieved in the concentration range χBi ∈ (0.1) with a step of the atomic fraction of 0.1. The measuring electrode consisted in Bi-Sn alloy with various compositions and the reference electrode was made from pure Bi.

Due to the development of this software in Java, the advantage of using it on different platforms is created. Java gives graphical possibilities and a graphical interface has been created that facilitates calculations that involve both metallic phases and make them feasible also for all users.

The software - TCBS was developed using the NetBeans IDE 8.0.2 in Java programming language for efficient evaluation of thermodynamic properties, and allows the calculation and analysis of the thermodynamic activities of Bi, Sn as

well as the comparison of the results obtained with the other results from the specialized literature.

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