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## ACTIVITY OF ZINC IN THE LIQUID Bi-In-Sn-Zn ALLOYS DETERMINED BY KNUDSEN METHOD

## POMIARY AKTYWNOŚCI CYNKU W CIEKŁYCH STOPACH Bi-In-Sn-Zn METODĄ EFUZYJNĄ KNUDSENA

The Knudsen effusion method was used for measurements of mass loss rate of liquid Bi-In-Sn-Zn alloys, in the temperature range from 572 to 768 K. The studies were carried out for the alloys with the ratio of Bi:In:Sn equal 2:6:2, 2:2:6 and 8:1:1. The obtained results were used for the calculation of zinc vapour pressure over liquid Bi-In-Sn-Zn alloys and next the activity of zinc in the Bi-In-Sn-Zn liquid phase. It was found that for the investigated alloys the activity of zinc shows the considerable positive deviation from the Raoult's law.

*Keywords:* quaternary system, activity of zinc, tin, indium, bismuth, zinc, vapour pressure, effusion method

Stosując efuzyjną metodę Knudsena pomierzono szybkość ubytku masy cynku z ciekłych stopów Bi-In-Sn-Zn, w zakresie temperatur od 572 do 768 K. Badania zostały przeprowadzone dla stopów o stosunku zawartości molowych Bi:In:Sn równym 2:6:2, 2:2:6 oraz 8:1:1. Wyniki badań zostały wykorzystane do obliczenia równowagowej prężności par cynku nad ciekłymi stopami Bi-In-Sn-Zn, a następnie aktywności cynku. Stwierdzono, że dla zbadanych stopów aktywność cynku wykazuje znaczne dodatnie odstępstwa od prawa Raulta.

## 1. Introduction

The quaternary Bi-In-Sn-Zn alloys seem to have two potential fields of application. First, those are considered as a promising lead-free solder material. Especially, the alloys based on the Sn-Zn eutectic can be used as the low temperature solders in electronic and electric devices and the peritectic alloys of the Sb-Sn as high temperature soldering material. Second, those alloys are widely tested as candidate materials for anodes in Li ion batteries. In addition, that system presents a rare case of low melting peritectically formed solid phase which makes that convenient as a test material of the fine details of mechanisms of peritectic transformations. Applying the alloys with Zn for soldering needs the protective atmosphere because of their high reactivity with oxygen or water. However, the profit of the lower temperature of the soldering process cannot be omitted when the huge number of electronic packages is produced. The interest of the Bi-In-Sn-Zn system phase diagram was focused mainly on the ternary systems containing zinc which could

be studied by EMF (electromotive force) or the partial pressure method.

To design Pb-free solder alloys which are drop-in replacements for 63Sn-37Pb (weight percent), Yoon *et al.* [1] carried out the thermodynamic studies on the Sn-Bi-In-Zn quaternary system in terms of phase equilibria. Based on the results of phase equilibria calculations, several specific alloy compositions were selected and analyzed using differential scanning calorimetry (DSC) measurements. DSC results were compared with thermodynamically calculated phase transition and melting temperatures. Liquidus temperatures were slightly higher than 200°C, however, solidus temperatures were lower, in the range of 130°C-180°C. Microstructures of as-cast and heat-treated alloys were examined through scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses.

The first extensive thermodynamic compilation of In-Sn-Zn, Bi-In-Zn and Bi-Sn-Zn systems can be found in the work of Moelans *et al.* [2]. They also tried to investigate Bi-In-Sn-Zn quaternary system by computer coupling of phase diagrams and thermochemical (Calphad)

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method [1] basing on the limited amount of experimental information provided by Yoon et al. [1]. Some Sn-rich alloys were analyzed by differential scanning calorimetry and their microstructure was examined using SEM and XRD.

Therefore, it is necessary to investigate the thermodynamic properties in the Bi-In-Sn-Zn quaternary system to improve the design of lead-free solders based on that system. It should be, additionally, noted that the activities of components of the lead-free solder systems Bi-In-Sn and Bi-In-Sn-Zn have been predicted at different temperatures by Tao [3]. But the activity of components in Bi-In-Sn-Zn system was not investigated by any experimental method up till now. So, it is the main reason that the measurements of the activity of zinc in the cited alloys were undertaken by the Knudsen method.

The obtained data will be used, in future, for the thermodynamic assessment of Bi-In-Sn-Zn system and for calculations of the phase equilibria.

## 2. Experimental

### 2.1. Sample Preparation

The experiments were carried out on samples of liquid Bi-In-Sn-Zn alloys. The liquid alloys were produced by melting pure components of the system directly prior to measurements. Any losses of mass which occurred during melting were attributed to zinc evaporation.

Bismuth used in the measurements was supplied by the ABCR GmbH & Co.KG and indium was delivered by Indium Corp., whereas zinc and tin were obtained from Alfa Aesar. Every used metal was of 99.999% purity.

### 2.2. The Equipment

The measurements of mass loss rate by the Knudsen method (KM) have been carried out on the “Mettler” TA1 thermobalance. Used in the course of the determination of effective surface of effusion orifice and partial pressure of zinc Pt/Pt-10%Rh thermocouples were calibrated at the melting point of pure copper, silver, lead, antimony and tin, and Ag-Cu and Ag-Sb eutectic alloys. All these metals were of purity higher than 99.99 mass percent.

Each Knudsen cell was assembled from a crucible of the diameter and height of 15 mm and a cover with conical effusion orifice. They were made of Ringsdorf’s high density graphite (SGL CARBON GmbH, Germany) and they were denoted by symbols from G1 to G4. The effective areas of the effusion orifices were determined by the indium evaporation by the earlier described procedure [4, 5].

### 2.3. Data Collection and Treatment

Measurement conditions of the mass loss rate in the Knudsen method are presented in Table 1. The first column contains symbols denoting the measurement series. In the next four columns the masses of bismuth, indium, tin and zinc used for the preparation of Bi-In-Sn-Zn samples are given. In the case of 2Bi6In2Sn-1b, 2Bi6In2Sn-1c, 2Bi2In6Sn-1b, and 2Bi2In6Sn-1c series there are no data on masses of metals (Table 1) because they respectively represent continuation of 2Bi6In2Sn-1a and 2Bi2In6Sn-1a. In last two columns the effective areas of effusion orifices ( $A_e$ ) and the cell symbol are shown, respectively. More detailed description of the methodology of experiments was given in work of Botor and Zajaczkowski [4].

TABLE 1

Characteristics of the experimental conditions

Series	$m_{Bi}$ , mg	$m_{In}$ , mg	$m_{Sn}$ , mg	$m_{Zn}$ , mg	Knudsen cell	
					$A_e \pm \sigma$ , mm <sup>2</sup>	Symbol
1	2	3	4	5	6	7
2Bi6In2Sn-1a	541.75	935.00	323.79	314.27	0.0478±0.00165	G1
2Bi6In2Sn-1b					0.794±0.0121	G2
2Bi6In2Sn-1c					4.395±0.0492	G3
2Bi2In6Sn-2a	554.39	300.65	943.49	322.70	0.0682±0.00163	G4
2Bi2In6Sn-2b					0.794±0.0121	G2
2Bi2In6Sn-2c					4.395±0.0492	G3
8Bi1In1Sn-3a	1614.15	123.68	135.47	332.62	0.0682±0.00163	G4

The composition of alloys and experimental temperatures were chosen in such a way that the zinc monomer was the main component of gas phase. Therefore, the relation describing the reaction proceeded in the system could be written as follows:



The measured values of mass loss rate were used to determine the vapour partial pressure of zinc over the Bi-In-Sn-Zn liquid phase by the Knudsen-Herz equation:

$$\bar{P}_{\text{Kn(Zn)}} = \left( \frac{dg}{dt} \right) \cdot \left( \frac{2\pi RT}{M_{\text{Zn}}} \right)^{1/2} \cdot A_e^{-1} \quad (2)$$

where:  $\bar{P}_{\text{Kn(Zn)}}$  is partial pressure of zinc,  $\left( \frac{dg}{dt} \right)$  is the mass loss rate of alloy sample due to effusion of zinc,  $R$  and  $T$  are the gas constant and absolute temperature of sample,  $M_{\text{Zn}}$  is the molar mass of zinc monomer,  $A_e = A \cdot W$  is the effective area of the effusion orifice as a product of geometrical area of an orifice ( $A$ ) and transmission probability of the orifice ( $W$ ).

The continuous measurement of the sample mass change allowed determining the mass of evaporated zinc and its current concentration in the sample.

### 3. Results and discussion

The results of measurement of the vapour pressure of zinc for the examined samples of the liquid Bi-In-Sn-Zn alloys, carried out by the Knudsen method and calculated according to Eq. 2 are presented in Fig. 1.

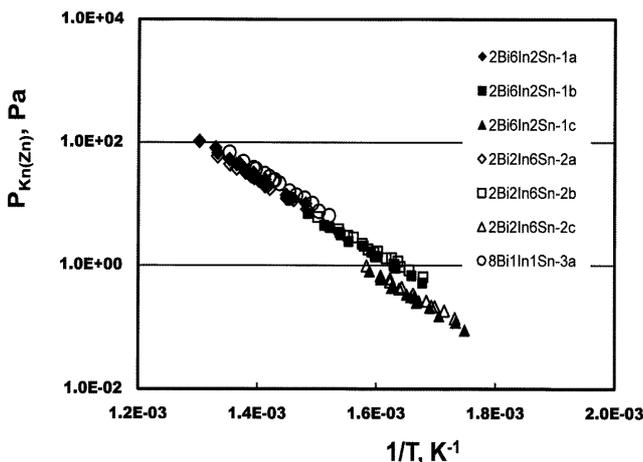


Fig. 1. The vapour pressure of zinc over liquid phase of the Bi-In-Sn-Zn system determined by the Knudsen method

The analysis of the zinc partial pressure given in Tables 3-5 allows to postulate that there is no influence of the concentration change of zinc on its partial pressure ( $\bar{P}_{\text{Kn(Zn)}}$ ). One can thus state the hypothesis that observed

shifts between experimental data for series 1a, 1b, and 1c, and also between experimental data for series 2a, 2b, and 2c are caused by the disturbance of equilibrium between liquid and gas phase by the effusion orifice. The reasons for such disturbance had been described for example by Cater [6, 7], and one of these reasons can be the lower rate of vaporization from surface of the sample than the rate of effusion for the equilibrium vapour pressure. To take into account such a disturbance of equilibrium, as for present zinc monomer, the following relation has been introduced into the description of the equilibrium vapour pressure of zinc monomer ( $\bar{P}_{\text{Eq(Zn)}}$ ) [6-9]:

$$\bar{P}_{\text{Eq(Zn)}} = \bar{P}_{\text{Kn(Zn)}} \cdot (1 + A_e/(\alpha \cdot A_s)) \quad (3)$$

where  $A_s$  and  $\alpha$  are the surface of the condensed phase and so called evaporation coefficient respectively. The evaporation coefficient  $\alpha$  renders possible to link the pressure measured by the Knudsen method with equilibrium pressure of zinc monomer over liquid Bi-In-Sn-Zn alloy. Therefore, the experimental data of zinc partial pressure calculated according to the Eq. (2) were in the next stage recalculated taking into account Eq. (3). The surface area of the condensed (liquid) phase was assumed to be equal to the surface area of the horizontal cross section of the graphite crucible of the Knudsen cell ( $A_s$ ). It was calculated from measurements of the crucible diameter to be 95.033 mm<sup>2</sup>. The effective area of the effusion orifice ( $A_e$ ) was taken from Table 1 and the evaporation coefficient  $\alpha$  was calculated. During these calculations it was assumed that the influence of zinc content change on  $\bar{P}_{\text{Eq(Zn)}}$  is negligible (in general, this assumption is not true, however in present calculations the accepted assumptions are the consequence of the fact that an effect of the zinc concentration on its partial pressure measured was not observed). In such a case the following equation could be applied:

$$\ln(\bar{P}_{\text{Kn(Zn)}} \cdot [1 + A_e/(\alpha \cdot A_s)]) = f(T) = A + B/T \quad (4)$$

The value of zinc evaporation coefficient ( $\alpha$ ), one of three parameters of Eq. 4, was calculated in the optimization process, separately for each of two alloys with the constant ratio of components (Bi/In/Sn = 2/6/2 and Bi/In/Sn = 2/2/6).

The obtained  $\alpha$  values were equal 0.025133 and 0.023923 for alloys Bi/In/Sn = 2/6/2 and Bi/In/Sn = 2/2/6, respectively, and the average value used in the next step of calculations of equilibrium pressure of zinc over liquid Bi-In-Sn-Zn alloys was  $\alpha = 0.02453 \pm 0.00061$ . Results of these calculations are presented in the fourth column of Tables 3-5.

The calculations of the zinc activity ( $a_{Zn}$ ) in studied quaternary alloys were carried out using the known relation:

$$a_{Zn} = \bar{P}_{Eq(Zn)}/P_{Zn}^0 \quad (5)$$

where:  $P_{Zn}^0$  is a zinc monomer pressure above pure liquid metal, which is assumed as a standard state for activity calculations.

The pressure of zinc monomer in standard state was calculated using a well known equation:

$$\Delta_r G_1^0 = -RT \cdot \ln(P_{Zn}^0) \quad (6)$$

which relates  $P_{Zn}^0$  to the standard Gibbs energy ( $\Delta_r G_1^0$ ) of reaction (1) by the following relation:

$$\Delta_r G_1^0 = -\Delta_r \Phi_1^0 \cdot T + \Delta_r H_1^0(298K) \quad (7)$$

in which  $\Delta_r \Phi_1^0$  is the free energy function (fef) of reaction (1) and  $\Delta_r H_1^0(298K)$  is the standard enthalpy of zinc sublimation.

A comparison of the right hand side of Eqs. (6) and (7) gives the following relation used in the calculation of equilibrium partial pressure of zinc over the liquid phase:

$$P_{Zn}^0 = 101325 \cdot \exp\left(\frac{(\Delta_r \Phi_1^0 \cdot T - \Delta_r H_1^0(298 K))}{(R \cdot T)}\right); \quad \text{Pa} \quad (8)$$

The function values of  $\Delta_r \Phi_1^0$ , were calculated for reaction (1) using the thermochemical data of liquid and gaseous zinc shown in Table 2, given by [10] and [11], respectively.

TABLE 2  
Standard molar Gibbs energy functions,  $\Phi^0(T)$ , of zinc

$\Phi^0(T) = -\frac{[G^0(T) - H^0(298K)]}{T}$ , J · mole <sup>-1</sup> · K <sup>-1</sup>		
Component	Zn(l) [10]	Zn(g) [11]
T, K	2	5
1	2	5
298.15	27.9178	160.8748
400.00	35.0386	161.6907
500.00	40.5524	163.2304
600.00	45.1523	164.9542
692.73	48.8630	166.5567
700.00	49.1363	166.6822
800.00	52.6800	168.3516
900.00	55.8732	169.9373
1000.00	58.7772	171.4394
1100.00	61.4389	172.8578
1184.00	63.5146	173.9414
1200.00	63.8950	174.1967

The value of standard enthalpy of zinc sublimation,  $\Delta_r H_1^0(298K) = 129.093 \pm 4.184$  kJ · mol<sup>-1</sup>, was taken from the work of Greenbank and Argent [12].

Values of the zinc activity calculated using Eqs. (5) and (8) are shown in Figs. 2a-c. From Tables 3-5 one can

find that the zinc activity in the quaternary Bi-In-Sn-Zn liquid alloys is characterized by positive deviations from ideal solution properties.

The activity of Zn in the quaternary Bi-In-Sn-Zn liquid alloys was calculated taking into consideration the model parameters from COST 531 ver. 3.0 database [13], which base on the assessments of Bi-In-Sn [14], Bi-Sn-Zn [15] and In-Sn-Zn [16] systems. The thermodynamic properties of Bi-In-Zn system were estimated from binary system parameters by Muggianu-Fitzner method [17, 18]. The ternary interaction parameters of Gibbs free energy of phases in ternary Bi-In-Zn were not yet assessed.

The calculated values of zinc activity in the quaternary Bi-In-Sn-Zn liquid alloys were compared at the same temperatures and concentrations with the experimental ones in Tables 3-5 and in Figs. 2a-c as a function of temperature. As it is seen from Fig. 2a-c the experimental data of this study differs from calculated in different extend. The experimental and calculated values

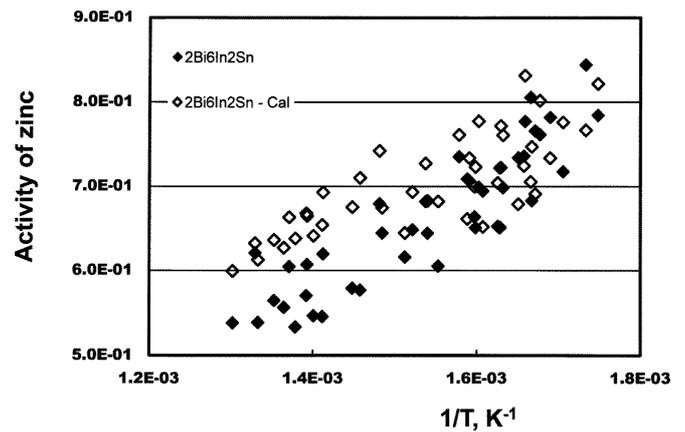


Fig. 2a. Dependence of zinc activity on the temperature in liquid (2Bi6In2Sn)+ Zn alloys, for different concentrations of Zn shown in Table 3. Black marks – experimental, white marks – calculated

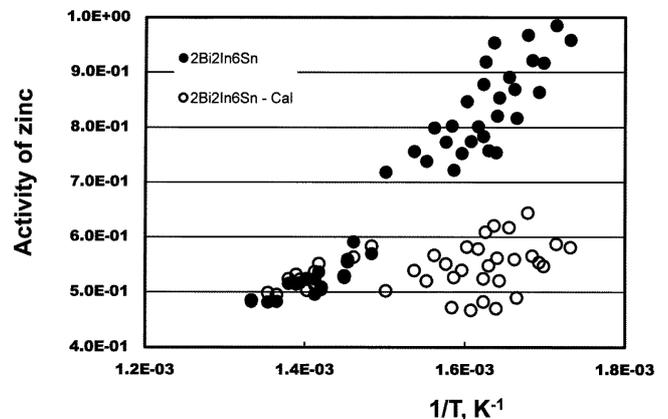


Fig. 2b. Dependence of zinc activity on the temperature in liquid (2Bi2In6Sn)+ Zn alloys, for different concentrations of Zn shown in Table 4. Black marks – experimental, white marks – calculated

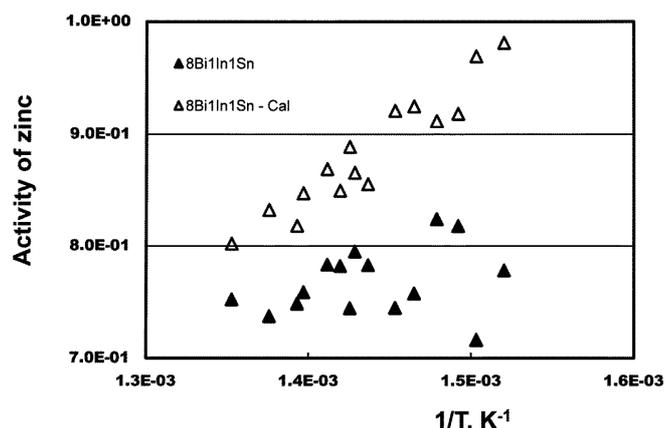


Fig. 2c. Dependence of zinc activity on the temperature in liquid (8Bi1In1Sn)+ Zn alloys, for different concentrations of Zn shown in Table 5. Black marks – experimental, white marks – calculated

of zinc activity in alloy with the ratio of components 2Bi6In2Sn + Zn are close to each other. However, for the other two alloys the observed deviations are somewhat larger. In the authors opinion there are two possible reasons of such deviation. First one can concern the value of the sublimation standard enthalpy of zinc used in calculations and the second one, which is more probable, concerns the lack of optimized ternary parameters describing the liquid state for Bi-In-Zn ternary solutions.

TABLE 3

Vapour pressure and activity of zinc in the Bi-In-Sn-Zn alloys

Set	Temperature, K	$(\bar{P}_{Kn(Zn)})$	$(\bar{P}_{Eq(Zn)})$	$a_{Zn}$	$x_{Zn}$
1	2	3	4	5	6
2Bi6In2Sn-1a	675.2	1.0199E+01	1.0408E+01	6.7949E-01	2.61675E-01
	707.9	2.4862E+01	2.5371E+01	6.1969E-01	2.60368E-01
	729.3	4.3836E+01	4.4734E+01	6.0459E-01	2.58521E-01
	752.1	8.1602E+01	8.3274E+01	6.2087E-01	2.55346E-01
	718.4	3.0687E+01	3.1315E+01	5.7032E-01	2.52778E-01
	686.1	1.2148E+01	1.2396E+01	5.7694E-01	2.51529E-01
	717.9	3.2216E+01	3.2876E+01	6.0704E-01	2.50192E-01
	739.2	5.3253E+01	5.4344E+01	5.6447E-01	2.48346E-01
	768.0	1.0469E+02	1.0683E+02	5.3804E-01	2.44365E-01
	750.1	6.7321E+01	6.8700E+01	5.3860E-01	2.41122E-01
	725.3	3.4728E+01	3.5439E+01	5.3327E-01	2.39085E-01
	732.8	4.4266E+01	4.5172E+01	5.5631E-01	2.37797E-01
	708.4	2.2198E+01	2.2653E+01	5.4551E-01	2.35957E-01
	690.5	1.3959E+01	1.4245E+01	5.7910E-01	2.33994E-01
713.9	2.5955E+01	2.6487E+01	5.4646E-01	2.32547E-01	
2Bi6In2Sn-1b	602.7	6.8400E-01	9.1707E-01	7.7722E-01	2.30579E-01
	633.5	2.0676E+00	2.7721E+00	7.3530E-01	2.28480E-01
	624.1	1.3945E+00	1.8697E+00	6.9927E-01	2.26991E-01
	650.3	3.4585E+00	4.6370E+00	6.8211E-01	2.24314E-01
	673.7	7.0239E+00	9.4172E+00	6.4439E-01	2.19401E-01
	657.3	4.1535E+00	5.5687E+00	6.4840E-01	2.15201E-01
	613.6	9.7326E-01	1.3049E+00	7.2247E-01	2.12464E-01
	628.5	1.6605E+00	2.2263E+00	7.0667E-01	2.08935E-01
	596.3	5.1722E-01	6.9347E-01	7.6148E-01	2.07471E-01
	612.6	9.0581E+00	1.2145E+00	6.9849E-01	2.05988E-01
	649.4	3.1581E+00	4.2342E+00	6.4428E-01	2.03092E-01
	625.5	1.3714E+00	1.8387E+00	6.5091E-01	2.00899E-01
	643.9	2.4584E+00	3.2961E+00	6.0521E-01	1.98002E-01
	661.3	4.4997E+00	6.0329E+00	6.1599E-01	1.94209E-01
626.0	1.4242E+00	1.9096E+00	6.6377E-01	1.90568E-01	
2Bi6In2Sn-1c	572.0	8.8400E-02	2.5509E-01	7.8428E-01	1.88427E-01
	599.8	2.4802E-01	7.1569E-01	6.8310E-01	1.86894E-01
	586.4	1.5030E-01	4.3372E-01	7.1747E-01	1.85516E-01
	615.1	4.3237E-01	1.2477E+00	6.5259E-01	1.83042E-01
	603.2	3.0694E-01	8.8573E-01	7.3602E-01	1.80845E-01
	629.5	8.0251E-01	2.3157E+00	7.0896E-01	1.77013E-01
	591.8	2.0556E-01	5.9316E-01	7.8188E-01	1.73966E-01
	576.9	1.1820E-01	3.4109E-01	8.4388E-01	1.72308E-01
	600.2	2.9837E-01	8.6100E-01	8.0560E-01	1.70644E-01
	622.1	5.9769E-01	1.7247E+00	6.9439E-01	1.67541E-01
	605.7	3.3765E-01	9.7434E-01	7.3410E-01	1.65061E-01
	598.3	2.6193E-01	7.5582E-01	7.6590E-01	1.63560E-01
	614.1	4.6060E-01	1.3291E+00	7.2204E-01	1.61210E-01

TABLE 4

Vapour pressure and activity of zinc in the Bi-In-Sn-Zn alloys

Serie	Temperature, K	$(\bar{P}_{Kn(Zn)})$	$(\bar{P}_{Eq(Zn)})$	$a_{Zn}$	$x_{Zn}$
1	2	3	4	5	6
<b>2Bi2In6Sn-2a</b>	684.6	1.1790E+01	1.2135E+01	5.9106E-01	2.69011E-01
	705.4	1.9855E+01	2.0436E+01	5.3598E-01	2.67768E-01
	674.2	8.2152E+00	8.4554E+00	5.6957E-01	2.66583E-01
	719.8	2.8583E+01	2.9419E+01	5.1413E-01	2.64138E-01
	724.8	3.2838E+01	3.3799E+01	5.1550E-01	2.62097E-01
	707.9	2.0826E+01	2.1435E+01	5.2355E-01	2.60199E-01
	688.1	1.2401E+01	1.2764E+01	5.5926E-01	2.58951E-01
	717.4	2.6817E+01	2.7601E+01	5.1673E-01	2.57107E-01
	738.7	4.4464E+01	4.5765E+01	4.8157E-01	2.53807E-01
	750.1	5.9833E+01	6.1582E+01	4.8280E-01	2.51114E-01
	732.8	3.8091E+01	3.9205E+01	4.8282E-01	2.48573E-01
	707.9	1.9716E+01	2.0293E+01	4.9566E-01	2.45934E-01
	690.0	1.2385E+01	1.2747E+01	5.2599E-01	2.44725E-01
	712.9	2.4038E+01	2.4741E+01	5.2488E-01	2.42596E-01
	704.0	1.7898E+01	1.8421E+01	5.0434E-01	2.40650E-01
<b>2Bi2In6Sn-2b</b>	611.2	1.1678E+00	1.5658E+00	9.5368E-01	2.38206E-01
	595.8	6.4416E-01	8.6366E-01	9.6767E-01	2.36700E-01
	615.1	1.3102E+00	1.7566E+00	9.1882E-01	2.35400E-01
	640.4	2.8752E+00	3.8550E+00	7.9907E-01	2.32649E-01
	604.2	8.3189E-01	1.1154E+00	8.9113E-01	2.30534E-01
	624.1	1.6891E+00	2.2646E+00	8.4698E-01	2.28436E-01
	650.8	3.8986E+00	5.2271E+00	7.5605E-01	2.24969E-01
	618.6	1.3034E+00	1.7475E+00	8.0132E-01	2.22354E-01
	634.5	2.2531E+00	3.0209E+00	7.7329E-01	2.19977E-01
	666.2	6.1698E+00	8.2722E+00	7.1836E-01	2.14985E-01
	644.4	3.0508E+00	4.0904E+00	7.3822E-01	2.10788E-01
	626.5	1.6446E+00	2.2050E+00	7.5262E-01	2.08647E-01
	609.7	9.4870E-01	1.2720E+00	8.2069E-01	2.07250E-01
	630.5	1.8235E+00	2.4449E+00	7.2202E-01	2.04898E-01
	613.6	1.0207E+00	1.3685E+00	7.5770E-01	2.03458E-01
<b>2Bi2In6Sn-2c</b>	601.7	3.4163E-01	9.8581E-01	8.6912E-01	2.00145E-01
	583.4	1.8198E-01	5.2511E-01	9.8500E-01	1.98486E-01
	593.8	2.6285E-01	7.5850E-01	9.2153E-01	1.96978E-01
	616.1	6.0424E-01	1.7436E+00	8.7821E-01	1.94005E-01
	577.4	1.3715E-01	3.9575E-01	9.5829E-01	1.91003E-01
	590.8	2.1798E-01	6.2900E-01	8.6381E-01	1.89413E-01
	608.7	4.4118E-01	1.2731E+00	8.5371E-01	1.87186E-01
	588.8	2.1306E-01	6.1482E-01	9.1682E-01	1.84892E-01
	631.5	9.7619E-01	2.8169E+00	8.0255E-01	1.79349E-01
	616.1	5.3913E-01	1.5557E+00	7.8358E-01	1.74708E-01
	622.1	6.6659E-01	1.9235E+00	7.7443E-01	1.71489E-01
	600.7	3.0857E-01	8.9043E-01	8.1675E-01	1.68406E-01
	610.2	4.1285E-01	1.1913E+00	7.5402E-01	1.65836E-01

TABLE 5

Vapour pressure and activity of zinc in the Bi-In-Sn-Zn alloys

Set	Temperature, K	$(\bar{P}_{Kn(Zn)}), \text{Pa}$	$(\bar{P}_{Eq(Zn)}), \text{Pa}$	$a_{Zn}$	$x_{Zn}$
1	2	3	4	5	6
<b>8Bi1In1Sn-3a</b>	688.1	1.6182E+01	1.6655E+01	7.4470E-01	3.36769E-01
	665.2	7.6029E+00	7.8253E+00	7.1617E-01	3.35421E-01
	701.5	2.4085E+01	2.4789E+01	7.4434E-01	3.32682E-01
	682.6	1.3931E+01	1.4339E+01	7.5753E-01	3.31241E-01
	657.8	6.4697E+00	6.6589E+00	7.7828E-01	3.29905E-01
	708.4	3.0971E+01	3.1876E+01	7.8335E-01	3.27794E-01
	726.8	4.8567E+01	4.9987E+01	7.3719E-01	3.24992E-01
	715.9	3.7015E+01	3.8097E+01	7.5869E-01	3.22102E-01
	739.2	6.8953E+01	7.0969E+01	7.5226E-01	3.17854E-01
	700.0	2.4633E+01	2.5353E+01	7.9510E-01	3.14210E-01
	676.1	1.2402E+01	1.2765E+01	8.2428E-01	3.12073E-01
	704.4	2.7593E+01	2.8400E+01	7.8221E-01	3.09117E-01
	670.2	1.0191E+01	1.0489E+01	8.1806E-01	3.07603E-01
	717.9	3.8596E+01	3.9724E+01	7.4853E-01	3.04533E-01
	696.0	2.1579E+01	2.2210E+01	7.8286E-01	3.02328E-01

#### 4. Summary

The partial pressure measurements of zinc over the Bi-In-Sn-Zn liquid solutions were conducted by the Knudsen method for three alloys with different ratio of Bi/In/Sn equal 2/6/2, 2/2/6, 8/1/1 between  $X_{Zn} = 0.161$  and 0.337 and in temperature range 572-768 K.

The calculation of zinc activity was performed taking into consideration the disturbance of the equilibrium state by the effusion orifice of the finite effective area.

The calculation of the zinc partial pressure over the liquid zinc was conducted using the standard sublimation enthalpy of zinc equal 129.093 kJ/mole [12].

It was found that the zinc activities measured and calculated from the thermodynamic parameter of COST 531 ver. 3.0 database [13] show deviations which can be probably the result of the lack of thermodynamic properties measurements which could have been used by the optimization of thermodynamic parameters describing the thermodynamics of liquid state of the Bi-In-Sn-Zn system.

Final verification of the activity measurements can be possible after evaluation of thermodynamic properties of liquid and solid solutions for the calculation of the Bi-In-Sn-Zn phase diagram what is predicted after bringing to an end another experimental study (EMF, metallographic, DTA) which are actually conducted.

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