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# THERMODYNAMIC PROPERTIES OF THE LIQUID Ag-Bi-Pb SOLUTIONS

# WŁASNOŚCI TERMODYNAMICZNE CIEKŁYCH ROZTWORÓW Ag-Bi-Pb

Employing the electrochemical cells with the solid electrolyte:

$$Pb,PbO\,|\,O^{-2}\,|\,air(p_{O_2} = 0.21\ atm)$$

and

$$Ag + Bi + Pb,PbO\,|\,O^{-2}\,|\,air(p_{O_2} = 0.21\ atm)$$

at first Gibbs free energy of formation of solid PbO was determined over the temperature range 848-1123K:

$$\Delta G^0_{f,PbO} = -215765 + 96.41 * T\ [J/mol].$$

Next, activities of lead in the liquid ternary Ag-Bi-Pb solutions along the cross-section $X_{Bi}/X_{Pb} = 1$, and for alloy compositions $X_{Ag} = 0.4, 0.5, 0.6, 0.7, 0.8$ were measured. Obtained data were used to estimate ternary interaction parameter in the equation describing thermodynamic properties of liquid solutions.

Consequently, ternary Ag-Bi-Pb phase diagram was recalculated taking into account the deviation from ideality of liquid ternary solutions.

Stosując ogniwa galwaniczne ze stałym elektrolitem typu

$$Pb,PbO\,|\,O^{-2}\,|\,air(p_{O_2} = 0.21\ atm)$$

oraz

$$Ag + Bi + Pb,PbO\,|\,O^{-2}\,|\,air(p_{O_2} = 0.21\ atm)$$

wyznaczono najpierw energię swobodną tworzenia stałego tlenku PbO w zakresie temperatur 848-1123K:

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** INSTYTUT METALURGII I INŻYNIERII MATERIAŁOWEJ PAN IM. ALEKSANDRA KRUPKOWSKIEGO, 30-059 KRAKÓW, UL. REYMONTA 25

$$\Delta G^0_{f,PbO} = -215765 + 96.41 * T \text{ [J/mol]}.$$

Następnie wyznaczono aktywności ołowiu w ciekłych stopach potrójnych Ag-Bi-Pb dla składów $X_{Ag} = 0.4, 0.5, 0.6, 0.7, 0.8$ przy stałym stosunku składów $X_{Bi}/X_{Pb} = 1$. Otrzymane wyniki użyto do wyznaczenia potrójnego parametru oddziaływania w równaniach opisujących właściwości termodynamiczne ciekłej fazy metalicznej. Tak wyznaczone zależności zastosowano w obliczeniach potrójnego układu równowagi biorąc tym samym pod uwagę odstępstwo właściwości roztworów potrójnych od stanu idealnego.

## 1. Introduction

The process of silver production from slimes, left after copper electrochemical refining is in principle based on the subsequent reduction and oxidation stages. The resulting distribution of solutes between silver phase and the slag phase is dependent on both temperature and oxygen partial pressure. During this particular process conducted in Kaldo furnace it was observed that depending on conditions:

- bismuth tends to accumulate in the metallic phase,
- antimony is gathered in the form of the oxide in the slag phase,
- antimony may appear as an impurity in obtained selenium, which is a by-product of silver production.

In order to explain this behavior and to describe the conditions of impurities distribution between metallic and the slag phases at fixed temperature and oxygen partial pressure, activities of components in both phases must be known. Consequently, thermodynamic properties of the silver multicomponent alloy must be described, for at least the quaternary Ag-Bi-Sb-Pb solutions. However, before reliable model for such a quaternary solution will be developed, thermodynamic data for, first binaries, and then ternaries, should be somehow verified. In the previous paper [1] we checked our experimental technique investigating activities in binary Ag-Bi liquid solution. Then, this technique was successfully applied to the study of liquid Ag-Sb solutions [2]. In this paper activities of lead in ternary Ag-Bi-Pb liquid solutions will be measured experimentally, and having description of the liquid phase, calculated phase equilibria will be checked by comparing them with known equilibrium data. The complete phase diagram Ag-Bi-Pb was obtained by computer optimization by Krieg and Lukas [3]. However, these calculations were made by using thermodynamic data and phase equilibria only for binary systems, and taking into account only DTA measurements of ternary liquidus temperatures. We found to our surprise that no reliable thermodynamic data for the liquid ternary phase exist. Results of calorimetric measurements given by Zimmermann [4] are confusing, and due to a strange choice of experimental compositions almost impossible to use. Thus, new measurements on ternary solutions should help to refine the description of the liquid ternary phase.

## 2. Experimental

*Materials*

Metallic silver was obtained from POCh Gliwice, bismuth was obtained from Koch-Light Laboratories U.K and lead was obtained from ZMR SKAWINA. They were 99.99%, 99.999% and 99.9999% pure, respectively. Lead oxide, PbO was obtained from International Enzymes Limted (UK) and was 99.9% pure. Closed at one end CSZ solid electrolyte tubes (length 50 mm, outside diameter 8 mm) were supplied by the Frialit-Degussit (Mannheim, Germany).

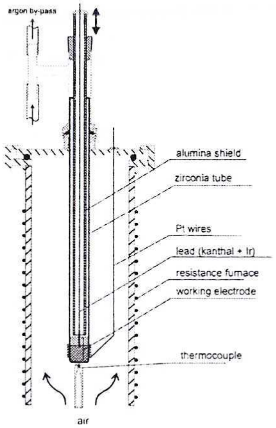

Fig. 1. Schematic diagram of the cell assembly

*Technique*

A schematic representation of the cell assembly is shown in Fig. 1. The tube of solid zirconia electrolyte contained about 2 g of metallic alloy of a chosen composition and air flowed in the outer furnace compartment. Alloys of Ag + Bi + Pb were prepared separately from pure metals by melting weighed amounts of silver, bismuth and lead in the silica capsules evacuated and sealed under vacuum. The leads from the liquid electrodes of the galvanic cell were made of piece of Iridium wire connected to Kanthal wire. Platinum wire was used as a connection to the outer part of the electrolyte tube's bottom, which was flushed with dry air, acting as the reference electrode. The working electrode was flushed inside the electrolyte tube with purified argon, and the whole cell was put into the constant temperature zone of the vertical resistance furnace. Temperature was controlled by Eurotherm controller, and EMF's were measured by high-resistance Keithley 2000 multimeter. To check reproducibility of the cell performance within temperature range 800-1100 K, measurements were carried out on both heating and cooling cycles. To achieve higher accuracy of EMF measurements a computer-controlled procedure was used, and a typical measurement's output is shown in Fig 2. Reading command was sent from computer to multimeter every 30 seconds, and within about 2 seconds 200 quick EMF readings were taken, the average value was calculated by multimeter and sent back to the computer as a single point shown in Fig 2. After a number of points were recorded, they were approximated by a regression line and its slope was analysed. If the curve was approaching horizontal position, another average value was calculated and plotted as a single EMF point shown in Fig. 3.

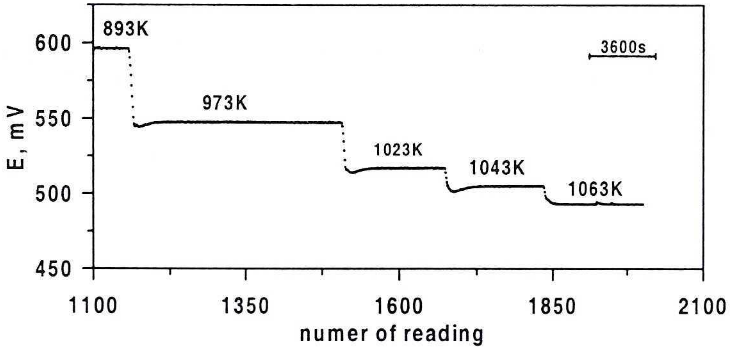

Fig. 2. Part of typical measurment output data

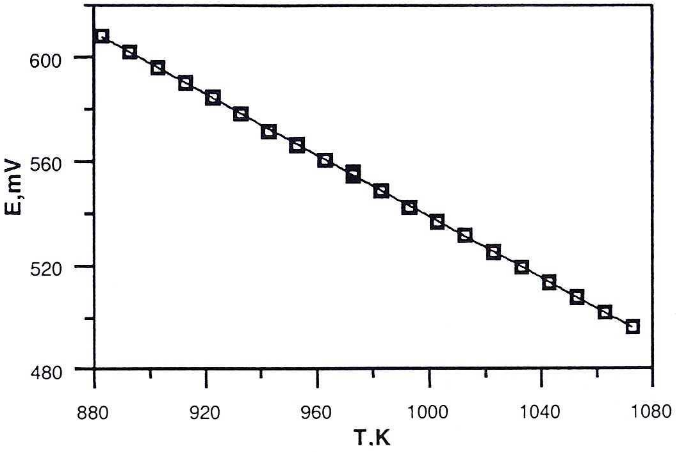

Fig. 3. A typical plot of the variation of EMF with temperature recorded for alloy $X_{Ag}$ = 0.6, and $X_{Bi}/X_{Pb}$ = 1

*Principle*

To determine the lead activity in liquid Ag-Bi-Pb alloys the EMF of the cell I:

$$Ir,Ag_XBi_{(1-X)/2}Pb_{(1-X)/2},PbO\,|\,O^{-2}\,|\,air,Pt \qquad \text{I}$$

was measured in the temperature range 875–1075 K. The cell scheme is written in such a way that the right-hand electrode is positive. For galvanic cell I the electrode reactions are:

a) at the right electrode:

$$\frac{1}{2}O_2 + 2e \Rightarrow O^{-2} \tag{1}$$

b) at the left electrode:

$$O^{-2} + \underline{Pb}_{(L)} \Rightarrow PbO_{(S)} + 2e. \tag{2}$$

Consequently, the overall cell I reaction is:

$$\frac{1}{2}O_2 + \underline{Pb}_{(L)} \leftrightarrow PbO_{(S)}. \tag{3}$$

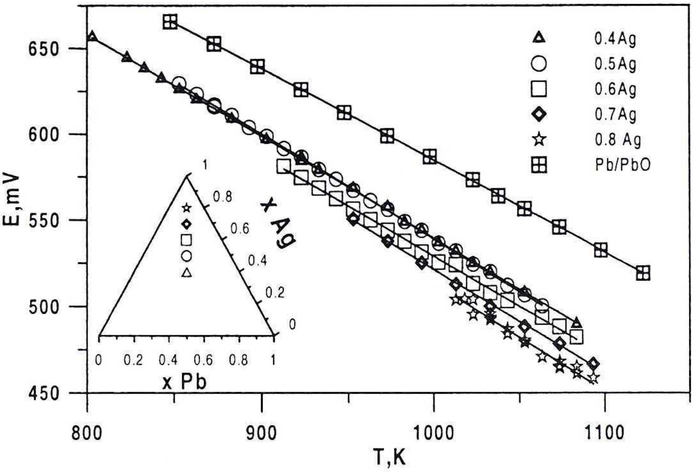

Fig. 4. Temperature dependence of EMF for liquid Ag-Bi-Pb where $X_{Bi}/X_{Pb} = 1$

For the reversible reaction (3) the change in Gibbs free energy can be derived as follows:

$$\Delta G = -2FE = \mu_{PbO} - \mu_{Pb} - \frac{1}{2}\mu_{O_2} \tag{4}$$

$$= \Delta G^0_{f(PbO)} - RT\ln(a_{Pb}) - \frac{1}{2}RT\ln(p_{O_2}),$$

where

$$\Delta G^0_{f,PbO} = -2FE^0 + {}^1/_2 RT\ln p_{O_2} \tag{5}$$

in the case of pure lead.

If the same air reference electrode is used for both pure lead and the alloy, terms with $\ln p_{O2}$ will cancel each other and after combining equations (4) and (5) the following expression for the activity of lead in the alloy with silver and bismuth can be derived:

$$\ln a_{Pb} = \left(\frac{2F}{RT}\right) \cdot \left(E - E^0\right), \tag{6}$$

where: $F$ is the Faraday constant, $T$ is the absolute temperature, and $R$ is the gas constant.

constant.

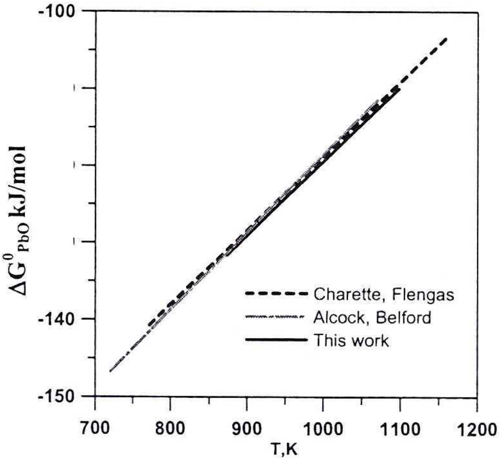

Fig. 5. Gibbs energy change for the reaction $\frac{1}{2}O_2 + \underline{Pb}_{(L)} \leftrightarrow PbO_{(S)}$ as a function of temperature

## 3. Results

Electromotive force values obtained in this work are shown in Fig. 4. Results of EMF measurements were treated by least-squares analysis. They are represented by equations given in Table 1. At first, we determined the free energy of formation of PbO from pure Pb

TABLE 1

Experimental data for the liquid Ag-Bi-Pb system

| **E[mV] = a + b*T** | | | |
|---|---|---|---|
| **$x_{Ag}$** | **$x_{Bi} = x_{Pb}$** | **a** | **b** |
| 0,8 | 0.1 | 1142,8 | -0,6293 |
| 0,7 | 0.15 | 1122,6 | -0,6012 |
| 0,6 | 0.20 | 1109,6 | -0,5805 |
| 0,5 | 0.25 | 1149,7 | -0,6107 |
| 0,4 | 0.30 | 1132,4 | -0,5929 |
| **Pb/PbO** | | 1118.1 | -0.5332 |

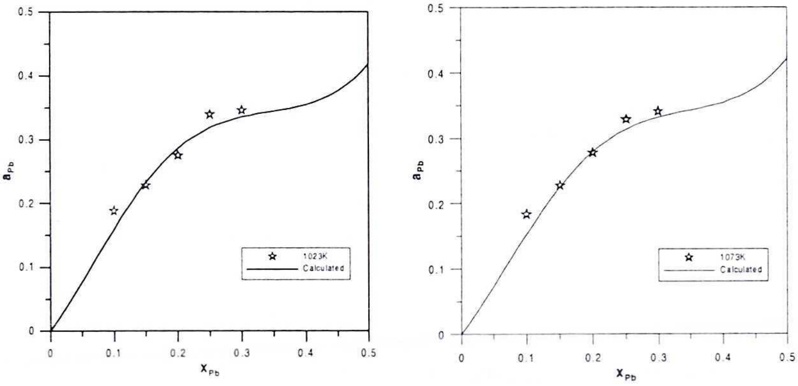

Fig. 6. Activities of Pb at 1023 and 1073 K

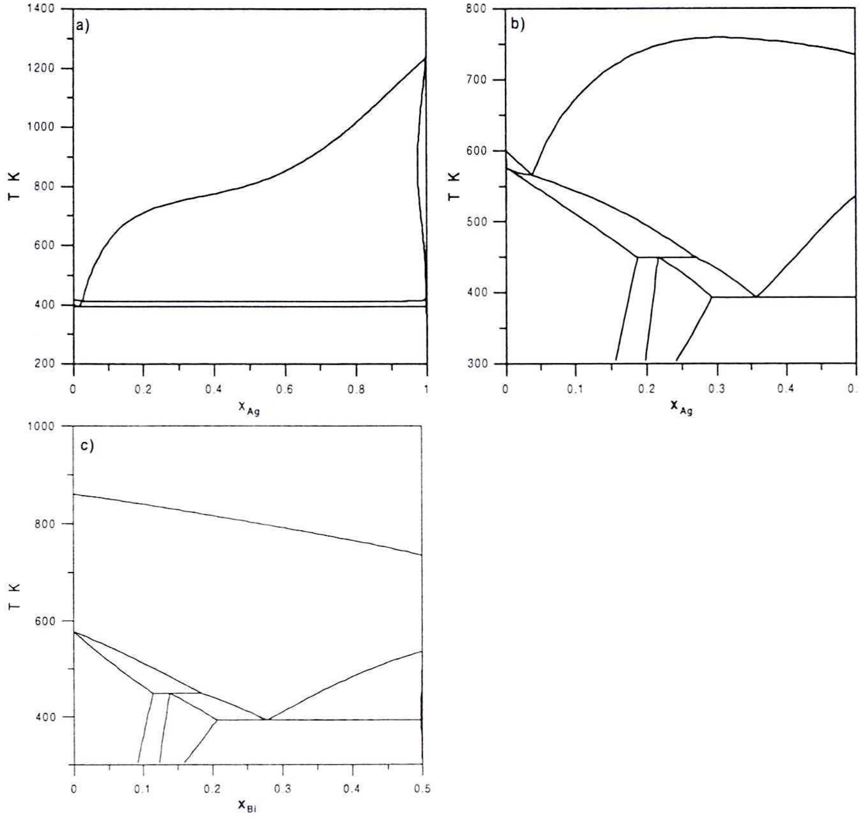

Fig. 7. Calculated vertical section of the Ag-Bi-Pb ternary system at (a) Bi : Pb = 1; (b) Ag : Bi = 1 and (c) $x_{Ag} = 0.5$

and oxygen. Measurements were conducted for this system in the temperature range 848–1123 K. Using E vs.T dependence given in Table 1 and equation 5 with $p_{O2} = 0.21$ atm for the air reference electrode, $\Delta G_f^0$ values for the formation of pure solid lead oxide were derived. They are shown and compared in Fig. 5 with those of Alcock and Belford [5] and Charette and Flengas [6]. It is clear that for solid PbO the results obtained in this work are in good agreement with those reported in both previous studies.

Since the temperature range covered by our experiments with alloys did not exceed the melting point temperature of pure solid PbO, the activities of lead were obtained directly from measured EMS's given in Table 1 with the use of eq. 6. Activities of lead derived in this manner are shown as a function of Pb mole fraction for two temperatures 1023 K and 1073 K in Fig. 6. For $X_{Pb} = 0.5$ activity of lead in binary Pb-Bi solution was accepted after Yoon and Lee [7]. Having the experimental data for ternary solution, the description of the thermodynamic properties of liquid solutions was carried out in the following manner: Using the model of substitutional solutions for the description of the liquid phase one can express the Gibbs free energy of the solution in the following form:

$$\begin{gathered} G_m = x_{Ag}\, G^o{}_{Ag} + x_{Bi}\, G^o{}_{Bi} + x_{Pb}\, G^o{}_{Pb} \\ + RT(x_{Ag} \ln x_{Ag} + x_{Bi} \ln x_{Bi} + x_{Pb} \ln x_{Pb}) + {}^{ex}G_m. \end{gathered} \tag{7}$$

Parameters $G_i^0$ denote free energy of pure component "i" and for the present calculations their values were taken from SGTE database [8]

Parameter ${}^{ex}G_m$ consists of two terms: first, obtained from Muggianu model [9], and second describing ternary interaction terms:

$${}^{ex}G_m = \sum_{i=1}^{2} \sum_{j=i+1}^{3} \left[ \frac{x_i x_j}{V_{i,j}\ V_{j,i}} \right] \cdot {}^{ex}G_{i,j} + x_{Ag}\, x_{Bi}\, x_{Pb} \cdot L_{AgBiPb}, \tag{8}$$

where $${}^{ex}G_{i,j} = x_i \cdot x_j \cdot \sum_{k=0} {}^{k}L\, (x_i - x_j)^k \tag{9}$$

$$V_{i,j} = \frac{1 + x_i - x_j}{2} \quad \text{and} \quad V_{j,i} = \frac{1 + x_j - x_i}{2}. \tag{10}$$

Accepting the description of respective binary systems after Yoon and Lee [7], Gąsior et al [1], and B.-Z. Lee et al [10] as well as the results of our measurements given in this work, the ternary parameters were assessed using Parrot module of ThermoCalc software by fitting both: our own thermodynamics activity data and constitutional data taken after Zimmermann [4]. The final set of data describing phase equilibria in the ternary system is given in Table 2.

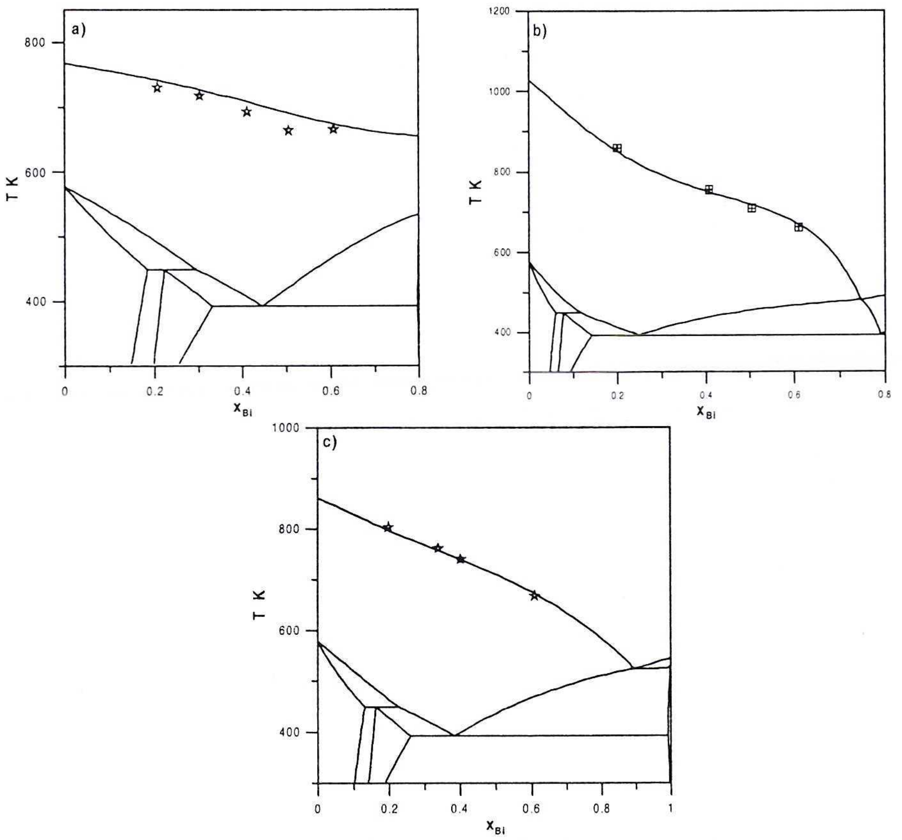

Fig. 8. Comparison of the calculated vertical sections with the experimental values (★) obtained by Zimmermann [4] in Ag-Bi-Pb ternary system at (a) $x_{Ag} = 0.2$; (b) $X_{Pb} = 0.2$ (c) Ag : Pb = 1

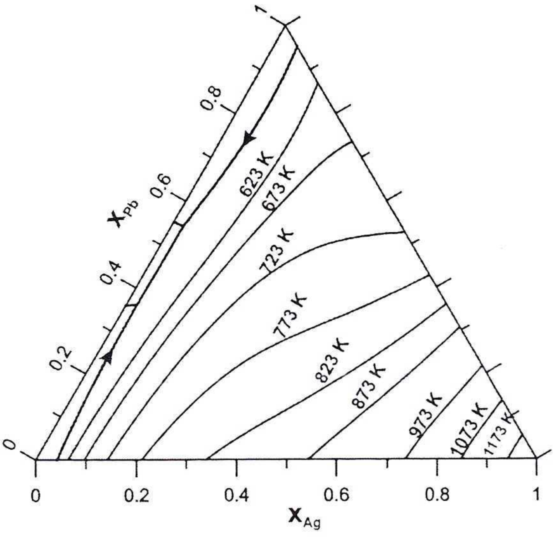

Fig. 9. Calculated liquidus projections of the Ag-Bi-Pb ternary system

TABLE 2

Interaction parameters (J mol$^{-1}$) of stable phase of the Ag-Bi, Ag-Pb, Bi-Pb and Ag-Bi-Pb systems

| Phase | Parameters | Reference |
|---|---|---|
| Liquid | ${}^{0}L^{liq}_{Ag,Bi} = 6966.56 - 4.4172 * T$<br>${}^{1}L^{liq}_{Ag,Bi} = -6580.41 + 1.5491 * T$<br>${}^{2}L^{liq}_{Ag,Bi} = -1942.3$ | [1] |
| | ${}^{0}L^{liq}_{Ag,Pb} = 13330.32 - 6.2127 * T$<br>${}^{1}L^{liq}_{Ag,Pb} = -1449.03 - 1.05718 * T$<br>${}^{2}L^{liq}_{Ag,Bi} = -2089.13$ | [11] |
| | ${}^{0}L^{liq}_{Bi,Pb} = -4807.37 - 1.25 * T$ | [8] |
| | ${}^{0}L^{liq}_{Ag,Bi,Pb} = x_{Ag} \cdot (0) + x_{Bi} \cdot (-94764.84 + 125.336 * T) + x_{Pb} \cdot (0)$ | This work |
| Fcc | ${}^{0}L^{fcc}_{Ag,Bi} = +24059.77 - 11.0254 * T$ | [1] |
| | ${}^{0}L^{fcc}_{Ag,Pb} = 30325.21 - 5.7434 * T$ | [11] |
| | ${}^{1}L^{fcc}_{Ag,Pb} = -3290.47$ | [11] |
| | ${}^{0}L^{fcc}_{Bi,Pb} = -5208.18 + 575 * T$ | [8] |
| Hcp | ${}^{0}L^{hcp}_{Ag,Bi} = 100 * T$<br>${}^{0}L^{hcp}_{Ag,Pb} = 100 * T$ | This work |
| | ${}^{0}L^{hcp}_{Bi,Pb} = -7388.9 - 0.68 * T$<br>${}^{1}L^{hcp}_{Bi,Pb} = 2.86 * T$ | [8] |

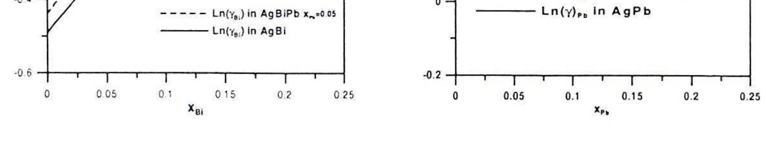

Fig. 10. Calculated activity coefficients of bismuth and lead in the liquid phase at 1273 K.
a) ln$g\gamma Bi$ in binary Ag-Bi solution (solid line) compared with ln$\gamma$Bi in ternary solution with $x_{Pb} = 0.05$ (dashed line).
b) ln$\gamma$Pb in binary Ag-Pb solution (solid line) compared with ln$\gamma$Pb in ternary solution with $x_{Bi} = 0.05$

For the calculations of the phase equilibria in the ternary system large positive parameters ${}^{0}L^{hcp}_{Ag,Bi}$ and ${}^{0}L^{hcp}_{Ag,Pb}$ have been assumed in order to ensure the negligible mutual solid solubility of bismuth an lead in the hcp phase.

The results of calculations of the phase equilibria in the ternary Ag-Bi-Pb system are shown in the subsequent Figures 7 through 9. The results of our calculations were compared with the results of DTA measurements of Zimmermann [4]. It is clear from Fig. 6 that good agreement between measured and calculated values is observed. Also, predicted course of activity vs. concentration dependence shown in Fig. 6 corresponds well to measured data.

## 4. Conclusions

The thermodynamic properties of ternary liquid solutions Ag-Bi-Pb were studied by high temperature galvanic cells with solid oxide zirconia electrolyte. In order to check the performance of our cell arrangement, we first determined $\Delta G^{0}_{f,\mathrm{PbO}}$ which is known accurately from previous measurements of Alcock and Belford [5] and Charette and Flengas [6]. The values we derived from EMF.'s of our cell I were found to be almost identical to those obtained in previous works [5, 6].This fact speaks for the reliability of our cell performance. Unfortunately, measurements with solid PbO as the oxide phase were possible only in the limited range of alloys concentration. For other cross-section the liquid oxide phase appeared. In such a case the distribution of components between the ternary alloy and the oxide phase is not known at present, which made the interpretation of obtained results impossible.

Activity values obtained in this study taken together with the results of DTA measurements taken by Zimmermann [4] as well as previously evaluated parameters for binary Ag-Bi [1], Ag-Pb [10] and Bi-Pb [7] systems let the set of parameters describing ternary system be optimized. Calculated phase equilibria are found to be in good agreement with the course of measured liquidus projections, which speaks in favor of our thermodynamic description. Recently, another description of this ternary system became available [12]. However, it operates with more adjustable parameters and avoids ternary interaction terms. We think that such a description of thermodynamic properties of the liquid solutions has no physical sense, though the formal fit of the existing data can be achieved.

The obtained description of the liquid phase enabled estimation of the mutual interaction between bismuth and lead in silver over dilute solution range.

Since in the dilute solution range in silver:

$$\ln\gamma_{\mathrm{Bi}} = \ln\gamma^{0}_{\mathrm{Bi}} + \varepsilon^{\mathrm{Pb}}{}_{\mathrm{Pb}}X_{\mathrm{Pb}} + \varepsilon^{\mathrm{Bi}}{}_{\mathrm{Pb}}X_{\mathrm{Bi}} + \dots \tag{11}$$

$$\ln\gamma_{\mathrm{Pb}} = \ln\gamma^{0}_{\mathrm{Pb}} + \varepsilon^{\mathrm{Bi}}{}_{\mathrm{Bi}}X_{\mathrm{Bi}} + \varepsilon^{\mathrm{Pb}}{}_{\mathrm{Bi}}X_{\mathrm{Pb}} + \dots \tag{12}$$

one can calculate the difference between the logarithms $\gamma$ at the infinite dilution for binary and ternary systems:

$$\{\ln\gamma_{Pb} - \ln\gamma^{0}_{Pb}\}\ XPb{-}{>}0 = \varepsilon^{Bi}_{Pb} X_{Bi} \tag{13}$$

$$\{\ln\gamma_{Bi} - \ln\gamma^{0}_{Bi}\}\ XBi{-}{>}0 = \varepsilon^{Pb}_{Bi} X_{Pb}. \tag{14}$$

At fixed temperature 1273K these differences are found to be 0.065 and 0.053 i.e. they are almost equal (see Fig. 10). This makes r.h.s. of equations (13) and (14) practically equal and with constant solute addition to the ternary system $X_{Bi} = X_{Pb} = 0.05$ one obtains:

$$\varepsilon^{Bi}_{Pb} \approx \varepsilon^{Pb}_{Bi} \approx 1.2. \tag{15}$$

Thus, calculated cross-interaction coefficients are approximately equal, which is compatible with Wagner's formalism [11]:

$$\varepsilon^{j}_{i} = \varepsilon^{i}_{j}. \tag{16}$$

This result suggests that the addition of the third component (either Bi or Pb) to the binary solution increases activity coefficient of the solute at fixed temperature. We believe that our work enriched the existing thermodynamic information about the properties of liquid phase in the ternary Ag-Bi-Pb ternary system as well as our knowledge about solute behavior in dilute solutions with silver.

## Acknowledgements

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