

Thermodynamic properties of liquid silver–indium alloys determined from e.m.f. measurements

Dominika Jendrzeczyk*, Krzysztof Fitzner

Laboratory of Physical Chemistry and Electrochemistry, Faculty of Non-Ferrous Metals, AGH University of Science and Technology 30 Mickiewicza Ave., 30-059 Krakow, Poland

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Abstract

The thermodynamic properties of the liquid Ag–In alloys were determined using solid oxide galvanic cells with zirconia electrolyte. The e.m.f.'s of the cells

Re + kanthal, $\text{Ag}_x\text{In}_{(1-x)}$, $\text{In}_2\text{O}_3//\text{ZrO}_2 + (\text{Y}_2\text{O}_3)//\text{NiO}$, Ni, Pt

were measured in the temperature range from 950 to 1273 K, and in the molar fraction from $x_{\text{In}} = 0.15$ to 1.0.

At first, the Gibbs free energy of formation of pure solid indium oxide, In_2O_3 , from pure elements was derived. Using values of the e.m.f.'s measured for the cell with $x_{\text{In}} = 1.0$, the following temperature dependence was obtained:

$$\Delta_f G_{\text{m,In}_2\text{O}_3}^0 (\pm 1000 \text{ mol}^{-1} \text{ J}) = -911570 + 313.10T$$

Next, the activities of indium were derived as a function of the alloy composition from measured e.m.f.'s. Activities of silver were calculated using Gibbs–Duhem equation. Also, using Darken's α -function formalism, activity coefficient of indium at infinite dilution in silver was calculated. These data taken together with the heat of mixing values which are available in the literature enabled the description of the thermodynamic properties of the liquid phase with Redlich–Kister polynomial expansion. Finally, the Ag–In phase diagram was recalculated using ThermoCalc software. The limiting value of the logarithm of the activity coefficient of indium in silver was also given as a function of temperature.

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1. Introduction

Under mounting environmental pressure on motor-car and electronic industries the necessity of the substitution of solder alloys containing lead became obvious worldwide. In short time three independent projects were created, namely:

- NCMS project in the United States in 1994–1997,
- IDEALS project in European Union in 1996–99,

- JEIDA and JWES projects in Japan, which ended in the year 2000.

Obtained results let seven groups of alloys be selected as potential candidates for the substitution of traditional alloys containing lead. It was found that in selected multicomponent alloys binary Ag–In system takes part as one of the possible binary contributions. Under COST 531 Action, which has developed basic research of thermodynamic properties of lead-free alloys, this particular system has been investigated in our laboratory.

The activities in the liquid silver–indium alloys were measured by applying various electrochemical cells.

* Corresponding author. Tel.: +48 12 617 41 25; fax: +48 12 633 23 16.
E-mail address: djendrzeczyk@interia.pl (D. Jendrzeczyk).

Mycielska et al. [1] measured activity of indium at $T = 1000$ K using liquid bromide electrolyte. Nozaki et al. [2] measured e.m.f.'s of the cells with liquid iodide electrolytes and reported activity of Indium at $T = 1100$ K. In turn Kameda et al. [3] carried out measurements with two types of cells using solid oxide and liquid chloride electrolyte. Predel and Schallner [4] obtained excess Gibbs energy for liquid alloy and its components using electrochemical cells with chloride electrolyte. Obtained data were used to calculate activity of indium at 1050, 1073, 1250 K. Alcock et al. [5] used combined measurements with Knudsen's cell and mass spectrometry.

They determined activity of silver and indium at 1300 K. Qi et al. [6] used similar method and gave indium activity at 1300 K. Calorimetric data of Kleppa were obtained at 723 K [7]. In this way $\Delta_{\text{mix}}H_m$ of liquid Ag–In alloy was obtained. Similarly, Castanet et al. [8] obtained $\Delta_{\text{mix}}H_m$ at 743 K and at 1280 K, Beja and Laffitte [9] at 1028 K, Itagaki and Yazawa [10] at 1243 K and Bienzle and Sommer [11] at 1500 K.

2. Experimental

2.1. Materials

Metallic silver was obtained from National Mint in Poland, while indium was obtained from Fluka AG Germany. They were 99.9999 and 99.99 mass% pure, respectively. Indium oxide, In_2O_3 , was obtained from POCh, Gliwice and was 99 mass% pure. Closed at one end YSZ electrolyte tubes (length 50 mm, outside diameter 8 mm) were supplied by the Yamari, Japan. Indium–silver alloys were prepared from pure metals by melting proper amounts of metals in the solid electrolyte tube during cell heating, argon 99.999 mass%.

2.2. Technique

A schematic representation of the cell assembly is shown in Fig. 1. The tube of the solid zircona electrolyte contained about 2 g of metallic alloy of a chosen composition. A small amount of pressed In_2O_3 was placed at the bottom inside YSZ tube. The kanthal wire with welded Re wire tip, kept inside the alumina shield acted as an electric contact with a liquid metal electrode. The platinum wire was connected to the outer part of the electrolyte tube. A solid electrolyte tube was inserted into an alumina crucible filled with Ni + NiO powder and sealed inside it with an alumina cement. The whole cell was placed inside the silica tube, which was suspended on an upper brass head, which closed the tube of a resistant furnace. The cell was kept in the constant temperature zone of the furnace under a flow of purified argon. The temperature inside the cell was maintained constant within ± 1 K which was achieved by using temperature controller Lumel type RE15. The e.m.f. of the cell was recorded by means of the digital multimeter Keithley 200. We have program which was written in Delphi. Thanks to it, e.m.f. values were read

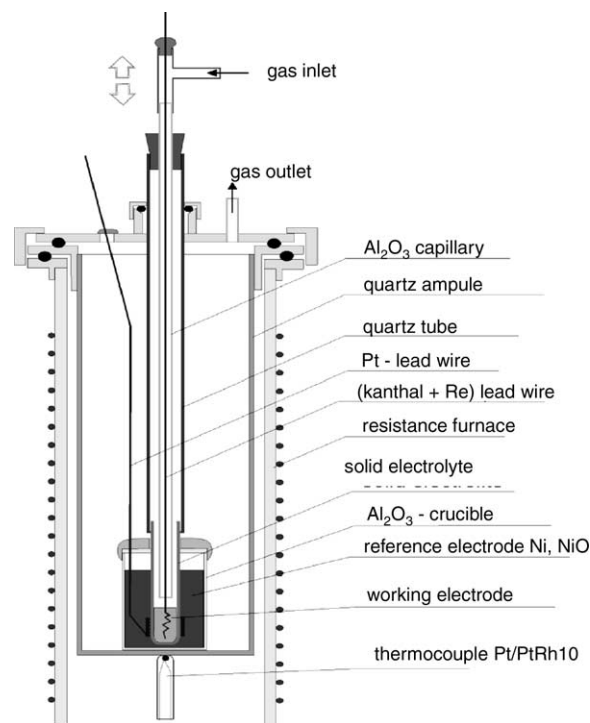


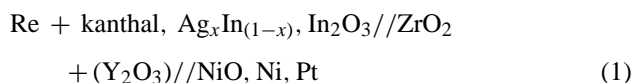
Fig. 1. Galvanic cell assembly.

out from Keithley straight to the computer and consequently we had very precise control of the e.m.f. change with temperature. The measurements were carried out at increasing and decreasing temperature for several days.

3. Results and discussion

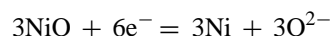
3.1. Results

In order to determine the indium activity in liquid Ag–In, the e.m.f. of the cell (I):

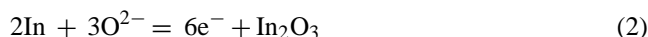


was measured in the temperature range from 950 to 1223 K. For galvanic cell (I) the electrode reactions are:

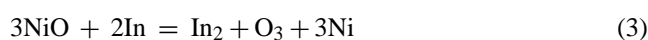
(a) at the RHS electrode:



(b) at the LHS electrode:



Consequently, the overall cell I reaction is:



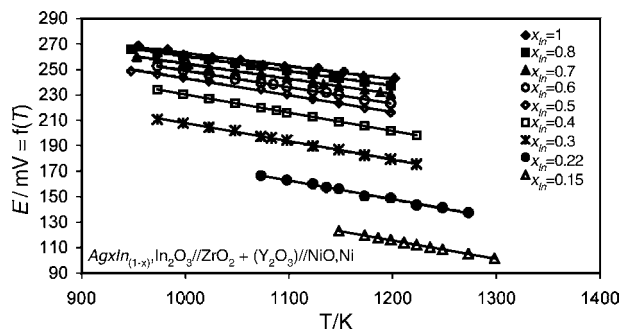


Fig. 2. Temperature dependence of the e.m.f.

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

$$\begin{aligned} \Delta_r G &= -6FE = \mu_{\text{In}_2\text{O}_3} + 3\mu_{\text{Ni}} - 2\mu_{\text{In}} - 3\mu_{\text{NiO}} \\ &= \Delta_f G_{\text{m}, \text{In}_2\text{O}_3}^0 - 3\Delta_f G_{\text{m}, \text{NiO}}^0 - 2RT \ln a_{\text{In}} \end{aligned} \quad (4)$$

If indium is in its pure, liquid state ($a_{\text{In}} = 1.0$) Eq. (5) takes the form:

$$-6FE^0 = \Delta_f G_{\text{m}, \text{In}_2\text{O}_3}^0 - 3\Delta_f G_{\text{m}, \text{NiO}}^0 \quad (5)$$

from which we can determine the change of Gibbs free energy of the reaction formation of pure solid In_2O_3 :

$$\Delta G_{\text{f}, \text{In}_2\text{O}_3}^0 = -6FE^0 + 3\Delta_f G_{\text{m}, \text{NiO}}^0 \quad (6)$$

Thus, from Eq. (6) the Gibbs free energy of formation of the solid In_2O_3 ($\Delta_f G_{\text{m}, (\text{In}_2\text{O}_3)}^0$), can be determined from E^0 measured as a function of temperature against the Ni, NiO reference electrode. Necessary $\Delta_f G_{\text{m}, \text{NiO}}^0$ values were accepted after Charette and Fregas [12].

e.m.f. values produced by the cell(I) in the range of temperature from 950 to 1223 K after the necessary thermo-e.m.f. Pt-(kanthal + Re) [13] corrections are shown in Fig. 2. The resulting linear equations obtained by the least square method, are presented in Table 1.

At first, from the results obtained for the equilibrium between pure liquid indium and indium oxide, the Gibbs free energy change for the reaction of formation of In_2O_3 was derived using Eq. (7). The obtained values of Gibbs free energy

Table 1
The temperature dependence of the e.m.f. of cell (I) corrected by thermo-e.m.f. (where σ is a standard deviation of E)

x_{In}	E (mV) = $a + b \cdot T$ (K)	σ
1.0	$359.03 - 0.0931T$	± 1.3
0.8	$375.44 - 0.1150T$	± 0.4
0.7	$373.10 - 0.1185T$	± 0.5
0.6	$379.24 - 0.1300T$	± 0.4
0.5	$376.10 - 0.1330T$	± 0.7
0.4	$374.78 - 0.1443T$	± 0.2
0.3	$3550.90 - 0.1431T$	± 0.5
0.22	$324.94 - 0.1474T$	± 0.5
0.15	$290.7 - 0.1458T$	± 0.1

yield the following temperature dependence:

$$\Delta_f G_{\text{m}, \text{In}_2\text{O}_3(\text{s})}^0 (\pm 1000 \text{ J mol}^{-1}) = -911570 + 313.10T \quad (7)$$

Our data, represented by Eq. (8) are shown in Fig. 3 and compared with the already published data [3,14–19]. A good agreement is found between results of different studies with the spread of results of the order of 17 kJ, which is about 3% of the measured value. Our results are in good agreement with those of Chatterji and Vest [15], Chatterji and Smith [17], Klinedinst and Stevenson [18] and Katayama et al. [19] while Kameda's values are bigger and those by Newns and Pelmore [14] smaller than the results of this study.

Next, by combining Eqs. (5) and (6) the following expression for the activity of indium in the alloy with silver can be derived:

$$\ln a_{\text{In}} = \frac{3F}{RT} (E - E^0) \quad (8)$$

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

Then, from the measured e.m.f.'s, the expression for the partial Gibbs free energy of indium in the alloy can be easily derived:

$$\Delta \bar{\mu}_{\text{In}} = RT \ln a_{\text{In}} = 3F(E - E^0) = 3F(\Delta a + \Delta bT) \quad (9)$$

if the linear dependence of the type $a + bT$ is assumed for temperature variation of the e.m.f.

Finally, using the well know relations, the partial entropy of indium can be obtained as:

$$\Delta_{\text{mix}} \bar{S}_{\text{In}} = - \left(\frac{\partial \Delta \bar{\mu}_{\text{In}}}{\partial T} \right)_p = -3F\Delta b \quad (10)$$

as well as the partial enthalpy:

$$\Delta_{\text{mix}} \bar{H}_{\text{In}} = \Delta \bar{\mu}_{\text{In}} + T\Delta \bar{S}_{\text{In}} = 3F\Delta a \quad (11)$$

Thus, having experimentally determined E as a function of T for various alloys, all partial thermodynamic functions for indium in the liquid alloy can be calculated.

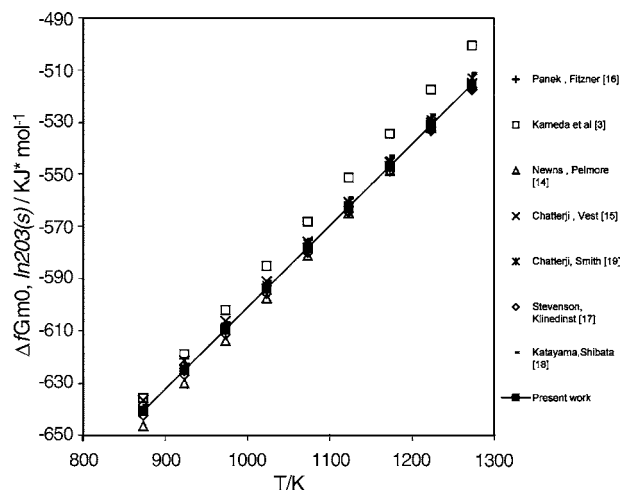


Fig. 3. Gibbs free energy of formation of the solid In_2O_3 .

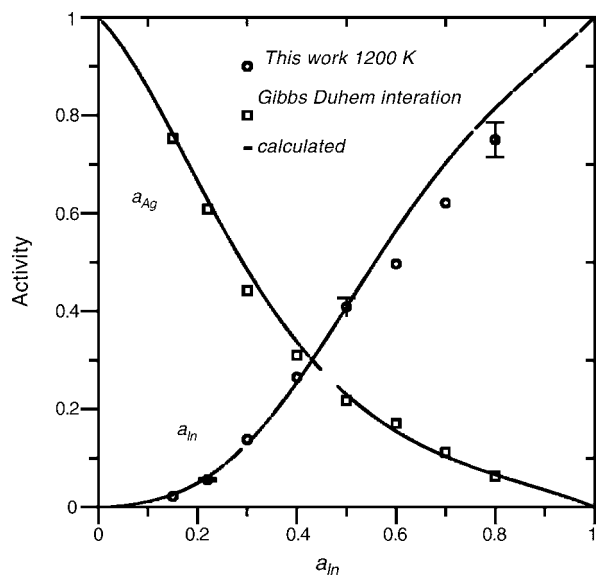


Fig. 4. Activities of components in Ag–In liquid alloys at $T = 1200$ K.

As an example, the activity of indium in the Ag–In alloys was calculated at 1200 K and it is shown in Fig. 4.

Corresponding activity of silver was calculated from γ_{In} Gibbs–Duhem equation. To do this, we derived at first the activity coefficient of indium at infinite dilution with silver.

We used Darken α -function method [20], which implies that $\ln \gamma_{\text{In}} = (1 - x_{\text{In}})^2$ plot is linear over certain concentration range. On this basis we could plot $\ln \gamma_{\text{In}}$ versus x_{Ag}^2 and extrapolate this plot to $\ln \gamma_{\text{In}}^0$ when $x_{\text{In}} \rightarrow 0$. This is shown in Fig. 5.

Having the value of $\ln \gamma_{\text{In}}^0 = -3.296$ at 1200 K one may derive $\ln \gamma_{\text{Ag}} = f(x_{\text{In}})$ at the same temperature using Gibbs–Duhem relationship:

$$\ln \gamma_{\text{Ag}} = - \int_{x_{\text{In}}=0}^{x_{\text{In}}} \left(\frac{x_{\text{In}}}{x_{\text{Ag}}} \right) d \ln \gamma_{\text{In}} \quad (12)$$

The $\ln \gamma$ values versus alloy concentration are shown in Fig. 6. Also, the activities of silver were calculated and are shown in Fig. 4.

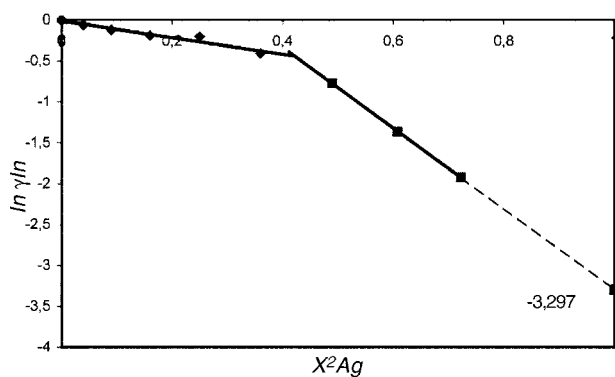


Fig. 5. Relation between $\ln \gamma_{\text{In}}$ and x_{Ag}^2 at 1200 K.

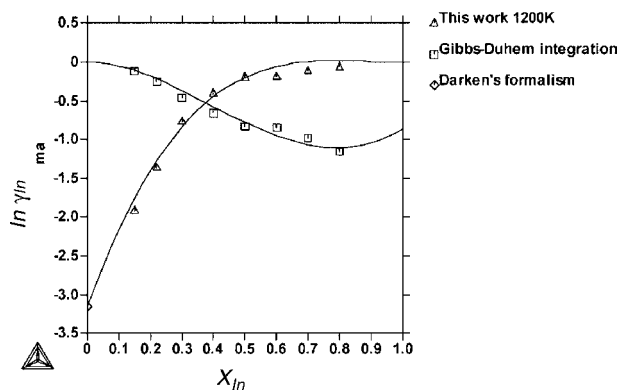


Fig. 6. Composition dependence of $\ln \gamma$ for both components at 1200 K.

In principle, one can calculate all partial functions in this way. However, since the split of the partial Gibbs free energy between enthalpy and entropy terms is always uncertain in electrochemical studies, we followed different approach. It is based on computer optimisation of thermodynamic data existing for a liquid phase.

We chose the integral heat of mixing data from the literature. Calorimetric data [7–9] of Kleppa at 723 K, Beja at 1028 K and Castanet at 723 and 1280 K were chosen. We accepted indium activities calculated at 1200 K from our own e.m.f. measurements, together with limiting values of $\ln \gamma^0$ obtained with α -function method. These data were used together to describe the thermodynamic properties of the liquid phase.

The results were described with Redlich and Kister equation [21] and using ThermoCalc software. It is assumed that the liquid solution phase is described by the disordered substitutional solution model and its excess Gibbs free energy is expressed by the following equation:

$$\Delta_{\text{mix}} G^{\text{xs}} = x_{\text{In}}(1 - x_{\text{In}}) \left[L_{\text{Ag,In}}^0 + (1 - 2x_{\text{In}})L_{\text{Ag,In}}^1 + (1 - 2x_{\text{In}})^2 L_{\text{Ag,In}}^2 + \dots \right] \quad (13)$$

in which x_{In} is the mole fraction of indium.

The expression for the partial excess Gibbs free energy of indium resulting from this model is:

$$\Delta_{\text{mix}} G_{\text{In}}^{\text{xs}} = (1 - x_{\text{In}})^2 \left[L_{\text{Ag,In}}^0 + (1 - 4x_{\text{In}})L_{\text{Ag,In}}^1 + (1 - 2x_{\text{In}})(1 - 6x_{\text{In}})L_{\text{Ag,In}}^2 + \dots \right] \quad (14)$$

Consequently, from these equations all thermodynamic function in the solution can be determined. Parameters $L_{\text{Ag,In}}^i$ are linearly dependent of temperature and are given in J/mol. Their values resulting from our calculations were found to be as follows:

$$L_{\text{Ag,In}}^0 = -13765.1 - 4.803T, \quad L_{\text{Ag,In}}^1 = -11431.5 - 0.031T, \quad L_{\text{Ag,In}}^2 = -1950.3 + 1.193T \quad (15)$$

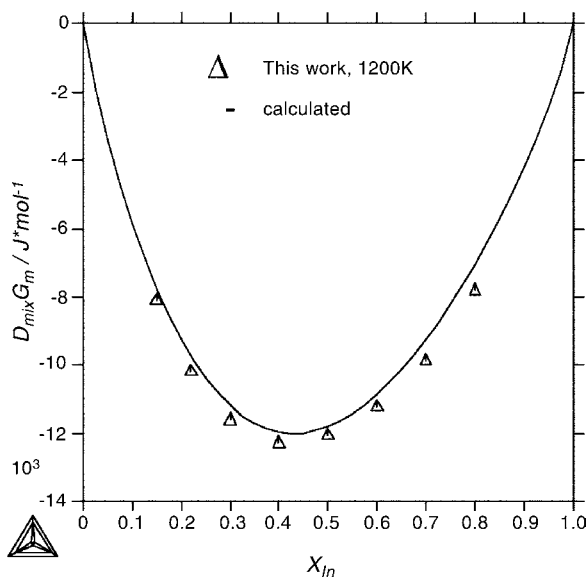


Fig. 7. Integral Gibbs energy of mixing in the liquid Ag–In system at 1200 K.

In Fig. 4 the activity of indium and silver obtained from our experiments are compared with the results of the model calculations. Integral Gibbs free energy of the solution calculated from obtained activities is shown in Fig. 7. Also, the determined from e.m.f.'s partial enthalpy and partial entropy functions of indium are shown in Figs. 8 and 9, and compared with the model calculations.

The logarithm of the activity coefficients of indium at infinite dilution was also derived for $x_{\text{In}} \rightarrow 0$ from Redlich–Kister formula obtained after optimisation. It is given by the following temperature dependence:

$$\ln \gamma_{\text{In}}^0 = -\frac{3266.8}{T} - 0.438 \quad (16)$$

4. Discussion

Electrochemical method proved to be successful in the determination of the thermodynamic properties of liquid silver

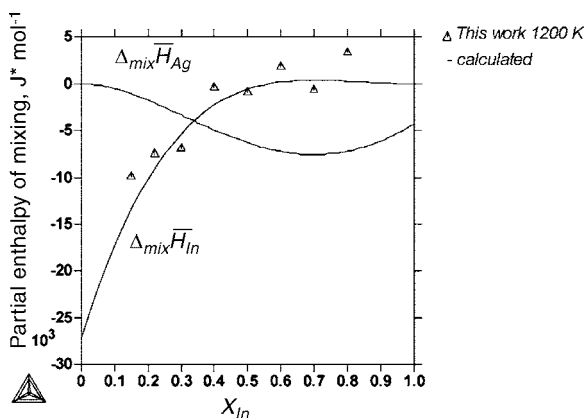


Fig. 8. Partial enthalpy of components in the liquid Ag–In system.

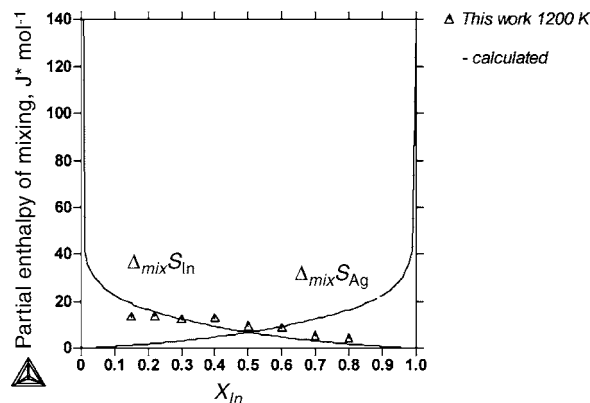


Fig. 9. Partial entropy of components in the liquid Ag–In system.

alloys with indium. The reliability of our cell performance was checked by $\Delta_f G_{\text{m, In}_2\text{O}_3}^0$ measurements of the solid indium oxide. The values obtained for the reaction of formation of solid indium oxide in this work are in good agreement with the results of previous studies [15–19]. In the present experimental temperature range they are all within ± 17 kJ, i.e. about 3% of the measured value.

Activities of indium in liquid Ag–In system were determined by Kameda et al. [3], who used e.m.f. cell identical with our cell (I). The only difference in the cell construction seem to be stainless steel instead of rhenium tip we used, and CSZ electrolyte instead of YSZ electrolyte applied in our cell. Unfortunately, direct comparison of the results is not possible since equations of e.m.f. versus temperature dependences are not given in Kameda's work.

Another check of experimental results one may do is to compare the value of $\ln \gamma_{\text{In}}^0$ at infinite dilution in different alloys. Since Ag–In and Ag–Sb systems are somewhat similar, one may also expect similar solute behaviour in silver. Indeed, the comparison of calculated $\ln \gamma^0$ values at 1200 K in these two systems yields $\ln \gamma_{\text{In}}^0 = -3.16$ and $\ln \gamma_{\text{Sb}}^0 = -2.77$, respectively. In turn, comparison of the heat of mixing in these two systems shows that $\Delta_{\text{mix}} H_{\text{m}}$ in Ag–In alloy is generally lower than in the Ag–Sb system, i.e. interactions between Ag and In atoms are stronger than between Ag and Sb atoms. This is compatible with the results of the comparison of $\ln \gamma$ values at infinite dilution.

Model calculations for the liquid phase were performed with Redlich–Kister formula. Similarly to other silver alloys like Ag–Bi [22], Ag–Sb [23], Ag–Pb [24], two-term L parameters should give satisfactory description of the thermodynamic properties of the liquid phase. Results of calculations obtained with L -parameters described by Eq. (16) are compared with experimental data and are shown in Figs. 4, 6–9. It is seen that calculated values are in reasonably good agreement with the experimental data. The observed discrepancy between calculated and measured activities of indium (Fig. 4) for high indium content can be explained by high uncertainty of measured values. They are calculated from the dif-

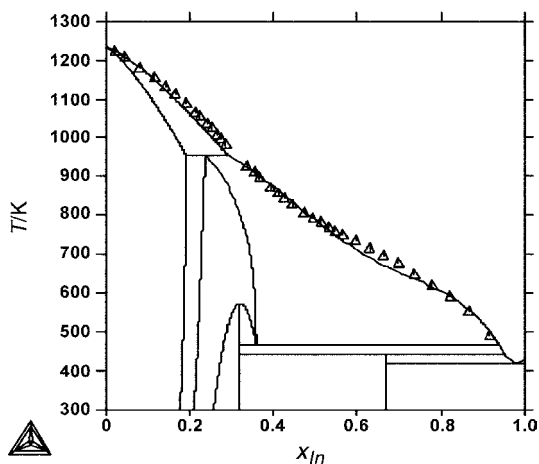


Fig. 10. Calculated phase diagram Ag–In.

ference of e.m.f.'s which is small and this leads to higher errors (Fig. 4).

Our results obtained for the liquid phase were incorporated into the COST 531 database, which is being developed at the University of Brno. Using this database the Ag–In phase diagram was calculated and is shown in Fig. 10. It is demonstrated that calculated phase diagram resembles closely that one determined experimentally. The only weak point of these calculations at present is still inadequate information concerning properties of the solid phases. Thorough literature search revealed that there is only one study concerning solid phases. Masson and Pradhan [25] determined activities of indium in the solid solution with silver using atomic absorption. No experimental data can be found for the ζ -phase. Thus, one cannot be sure if the existing discrepancy in the phase relations between calculated and experimentally determined phase diagram is due to the inadequate description of the liquid phase or it is a result of the missing information about the stability of the solid phase.

Concluding, it seems that our e.m.f. technique is precise enough to be safely used in the investigations of the liquid

solutions of the higher order systems containing silver and indium.

Acknowledgements

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References

- [1] E.P. Mycielska, J. Terpiłowski, K. Strożecka, *Arch. Hutnictwa* 8 (1963) 85.
- [2] T. Nozaki, M. Shimoji, K. Niwa, *Trans. JIM* 7 (1966) 52.
- [3] K. Kameda, Y. Yoshida, S. Sakairi, *J. Jpn. Inst. Met.* 45 (1981) 614.
- [4] B. Predel, U. Schallner, *Z. Metallkd.* 63 (1972) 341.
- [5] C.B. Alcock, R. Sridhar, R.C. Svedberg, *Acta Metall.* 17 (1969) 839.
- [6] G. Qi, M. Hino, T. Azakami, *Mater. Trans. JIM* 30 (1989) 75.
- [7] O.J. Kleppa, *J. Phys. Chem.* 60 (1956) 846.
- [8] R. Castanet, Y. Claire, M. Laffitte, *J. Chim. Phys.* 67 (1970) 789.
- [9] R. Beja, M. Laffitte, *C. R. Acad. Sci. Paris* 267C (1968) 123.
- [10] K. Itagaki, A. Yazawa, *J. Jpn. Inst. Met.* 32 (1968) 1294.
- [11] M. Bienzle, F. Sommer, *Z. Metallkd.* 85 (1994) 766.
- [12] G.G. Charette, S.N. Frengas, *J. Electrochem. Soc.* 115 (1968) 796.
- [13] B. Onderka, Ph.D. Thesis IMIM PAN Kraków (1994).
- [14] G.R. Newns, J.M. Pelmore, *J. Chem. Soc. A* (1968) 360.
- [15] D. Chatterji, R.W. Vest, *J. Am. Ceram. Soc.* 55 (1972) 575.
- [16] Z. Panek, K. Fitzner, *Thermochim. Acta* 97 (1986) 171.
- [17] D. Chattefji, J.V. Smith, *J. Electrochem. Soc.* 120 (1973) 889.
- [18] K.A. Klinedinist, D.A. Stevenson, *J. Chem. Thermodyn.* 5 (1973) 21.
- [19] I. Katayama, J. Shibata, Z. Kozuka, *J. Jpn. Inst. Met.* 39 (1975) 990.
- [20] L.S. Darken, *Trans. Met. Soc. AIME* 239 (1967) 81.
- [21] O. Redlich, A. Kister, *Ind. Eng. Chem.* 40 (1948) 345.
- [22] W. Gasior, J. Pstruś, A. Krzyżak, K. Fitzner, *J. Phase Equilibria* (2003) 24.
- [23] A. Krzyżak, K. Fitzner, *Thermochim. Acta* 414 (2004) 115.
- [24] B.Z. Lee, C.S. Oh, D.N. Lee, *J. Alloys Compd.* 215 (1994) 293.
- [25] D.B. Masson, S.S. Pradhan, *Metall. Trans.* 4 (1973) 991.