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# DIFFERENTIAL THERMAL ANALYSIS OF THE BINARY SYSTEM Pb–In

## RÓŻNICOWA ANALIZA TERMICZNA UKŁADU Pb–In

Results of thermodynamic analysis of Pb–In binary system are presented in this paper. Partial and integral molar quantities in the temperature interval 673—793 K were experimentally determined using quantitative differential thermal analysis. Obtained results were compared with literature data, and good agreement was noticed.


W pracy zaprezentowano wyniki analizy termodynamicznej układu Pb–In. Wyznaczono doświadczalnie funkcje termodynamiczne w zakresie temperatury 673 – K za pomocą ilościowej analizy termicznej różnicowej. Uzyskane wyniki dobrze się zgadzają z dostępnymi danymi literaturowymi.

## 1. Introduction

Pb–In alloys have often been the research subject [1, 2] among numerous lead alloys. Because of their relatively low melting temperatures, they are used as contact alloys for metal-glass or metal-ceramics connections.

There are a lot of data considering the phase diagram of this system, starting with works of K l e i n and V o l k [3] M o o r e [4] and V a l e n t i n e r [5] who did first investigations in Pb–In system using thermal analysis and $X$-ray analysis. Further researchers [6—10] continue with correct determination of phase boundaries, liquidus and solidus curves over the entire composition range, but the most complete assessment of the Pb–In phase diagram is given in the work of N a b o t and A n s a r a [11].

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Concerning the thermodynamic investigations of Pb–In binary system, there are a lot of literature data [12—16]. In H u l t g r e n ' s [12] and K u b a s c h e w - s k i ' s [13] book, data for partial and integral moral quantities are given for whole concentration range at the temperature of 673 K. Also, T e r p i l o w s k i and G r e g o r c z y k [14] obtained selected free mixing energies by performing EMF measurements. W i t t i g and S c h e i d t [15] determined enthalpies of mixing in this system, while S c h e i l and L u k a s [16] calorimetrically investigated the same thermodynamic parameters. S o m m e r, S u h and P r e d e l [17] obtained activities of lead and indium at 1000 K by K n u d s e n method, and S c h i u and M u n i r [18] performed vapor pressure measurements at 1070 K. N a b o t and A n s a r a [11] determined the interaction parameters of $G^{xs}$, derived from an optimization procedure using Lukas program.

Results of the quantitative DTA thermodynamic analysis for the whole concentration range in the temperature interval 673—973 K are presented in this paper and compared with existing thermodynamic data from literature.

## 2. Experimental

Quantitative DTA method was used for the experimental thermodynamic investigation of Pb–In binary system. Description of this experimental technique is reported in Refs [19—23].

Metallic Pb and In, used in experiments, were of p.a. purity. Calcinated p.a. pure $Al_2O_3$ was used as a referent material.

Compositions of the investigated samples are given in Table 1. All experiments were carried out in an air atmosphere. Volume of samples was 0.2 cm$^3$.

TABLE 1

Composition of the investigated samples

| sample | mass % | | $X_i$ | | m (g) | | m (total) |
|--------|------|------|--------|--------|--------|--------|-----------|
| | Pb | In | Pb | In | Pb | In | |
| U1 | 7.7864 | 92.213 | 0.0447 | 0.9553 | 0.1171 | 1.3869 | 1.504 |
| U2 | 16.702 | 83.298 | 0.1 | 0.9 | 0.2605 | 1.2992 | 1.5597 |
| U3 | 21.7248 | 78.275 | 0.1333 | 0.8667 | 0.3445 | 1.2311 | 1.5856 |
| U4 | 31.0887 | 68.912 | 0.2 | 0.8 | 0.5116 | 1.1339 | 1.6455 |
| U5 | 34.1589 | 65.841 | 0.2233 | 0.7767 | 0.5691 | 1.097 | 1.6661 |
| U6 | 54.608 | 45.392 | 0.4 | 0.6 | 0.9929 | 0.8253 | 1.8182 |
| U7 | 64.344 | 35.656 | 0.5 | 0.5 | 1.223 | 0.6777 | 1.9007 |
| U8 | 73.023 | 26.977 | 0.6 | 0.4 | 1.4324 | 0.5435 | 1.9759 |
| U9 | 87.832 | 12.168 | 0.8 | 0.2 | 1.8749 | 0.2597 | 2.1346 |
| U10 | 94.199 | 5.801 | 0.9 | 0.1 | 2.0961 | 0.1965 | 2.2926 |

## 3. Results and discussion

### a) Phase diagram determination

Considering literature data [11], Pb–In diagram exhibits an In-rich and an extended Pb-rich sample phase region in the solid state, while these phases are separated by an intermediate (αIn) phase.

Comparison between Pb–In phase diagram assessed by N a b o t and A n s a r a [11] and results obtained by DTA investigations in this paper, is shown in Fig. 1.
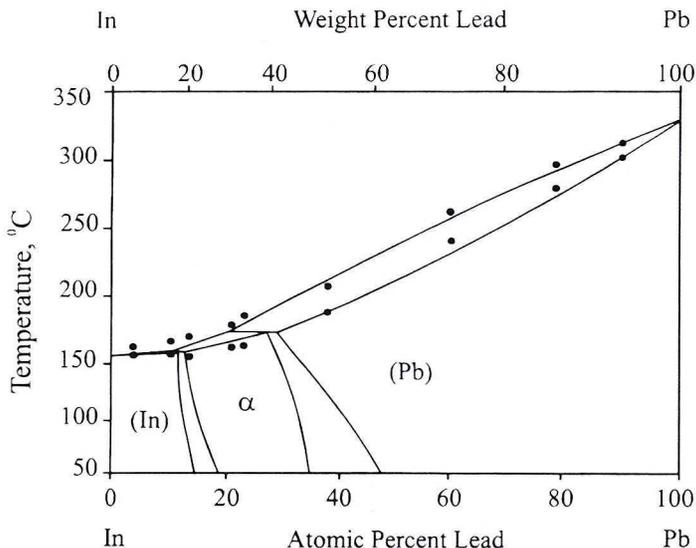


Fig. 1. The phase diagram of Pb–In system (lines — Nabot and Ansara [11]; dark points — this work)

### b) Determination of the calibration constant

According to the basic equation of the quantitative DTA:

$$m\Delta H_T^0 = gK_s \int_a^c \Delta T dT, \qquad (1)$$

where are: $m$ — sample mass, $\Delta H_T^0$ — the enthalpy of reaction, $gKs$ — calibration constant and $\int_a^c \Delta T dT = S$ — peak area, it was necessary to determine the value of calibration constant, $gKs$, which represents the equivalent factor betwen the enthalpy of reaction and the peak area. In order to obtain these values, DTA measurements for different masses of lead and indium were performed and $gKs$ — constants were determined from a slope of dependencies $m\Delta H_f/M = f(S)$ ($\Delta H_f$ — heat of fussion and $M$ — atomic weight for the responding metal) using statistic method of minimal squares. In this case, the values are 0.15058 J/mm² for lead and 0.136675 J/mm² for indium.

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Dependencies of the calibration constant on composition of binary system Pb–In are presented in Figure 2. Linear dependence of $gKs$ could be noticed, as was proved by earlier given conclusions for different binary systems [21—23].
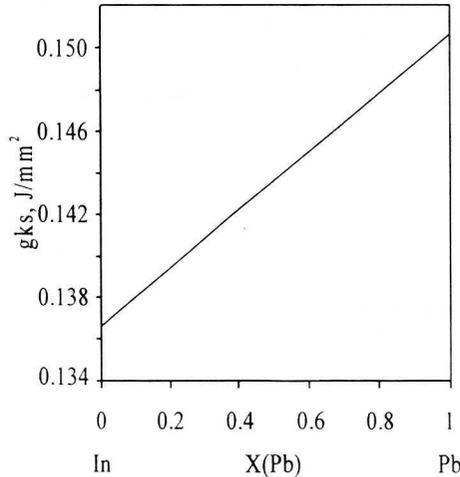


Fig. 2. Values of calibration constants, $gKs$ for Pb–In system

## c) Determination of mixing enthalpy in liquid and solid state

During the quantitative DTA experiments of any binary system, samples are melted two times. Considering the first melting, metal with lower melting temperature is melted, and first peak is registered on DTA curve. First peak area is proportional to the enthalpy of melting for this metal. With further heating, the second metal with higher melting temperature is melted and mixed in alloy. Then, a second peak is registered on DTA curve of the first melting. Second peak area is proportional to the enthalpy of melting for the second metal and mixing enthalpy of the alloy. Enthalpy needed for this melting is given as:

$$\Delta H_I = X_1 L_1 + X_2 L_2 + \Delta H_{liq}, \tag{2}$$

where are: $\Delta H_I$ — enthalpy of the first melting, $X_i$ — molar content of the component "$i$", $L_i$ — melting enthalpy of the component "$i$", and $\Delta H_{liq}$ — mixing enthalpy in liquid state.

After cooling, sample is melted for the second time, and new peak is registered on DTA curve. This peak area is proportional to he sum of pure metal enthalpy of melting, mixing enthalpy in liquid state and enthalpy of mixing for solid solutions. The expression responding to this case is given as:

$$\Delta H_{II} = X_1 L_1 + X_2 L_2 + \Delta H_{liq} - \Delta H_{sol} \tag{3}$$

where are: $\Delta H_{II}$ — enthalpy of the second melting and $\Delta H_{sol}$ — mixing enthalpy in solid state.

Mixing enthalpy in solid state, $\Delta H_{sol}$, presents difference between $\Delta H_I$ and $\Delta H_{II}$:

$$\Delta H_{sol} = \Delta H_I - \Delta H_{II}. \tag{4}$$

Using Eqs. (2—4), mixing enthalpies in liquid and solid state were determined. The results are presented in Fig. 3, and compared with literature data [15—16].
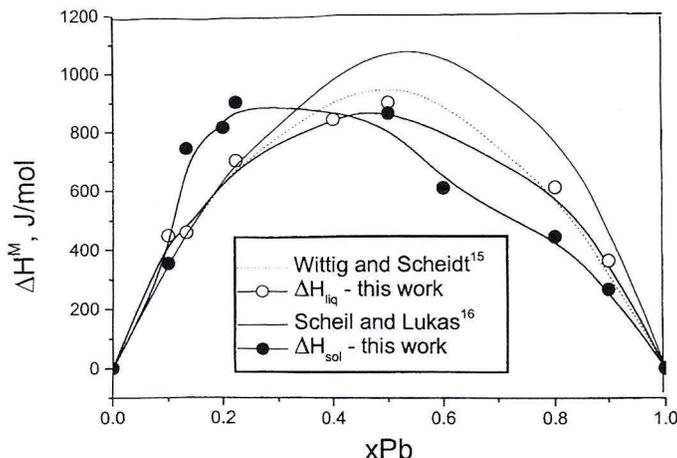


Fig. 3. Mixing enthalpies in liquid and solid state for Pb–In system in comparison with literature data

### d) Determination of other thermodynamic values

Beside obtained values for enthalpy of mixing in liquid state, values for mixing entropy are needed for further calculations. Certain simplification was done in this case, by using ideal mixing entropy, according to equation:

$$\Delta S_{id}^m = - R \left( x_1 \ln x_1 + x_2 \ln x_2 \right), \tag{5}$$

where are: $\Delta S_{id}^m$ — mixing entropy for ideal solution and $R$ — gas constant.

Next step was determination of Planck potential values for corresponding compositions of the investigated system and temperatures, which can be obtained using the following expression:

$$P_{i,x,T} = \Delta S_{i,x,T}^m - \left( \Delta H_{i,x,T}^m / T \right) \tag{6}$$

Tangent construction on Planck potential curve, presented as a dependence on composition, enabled the determination of $- R \ln a_{xt}$ term (Fig. 4).

Based on obtained data for $- R \ln a_{Pb}$ and $- R \ln a_{In}$, activities of Pb and In at different temperatures (673, 773, 873 and 973 K) were calculated. Further, activity coefficients, partial ad integral molar quantities at the investigated temperatures were determined and presented in Table 2.
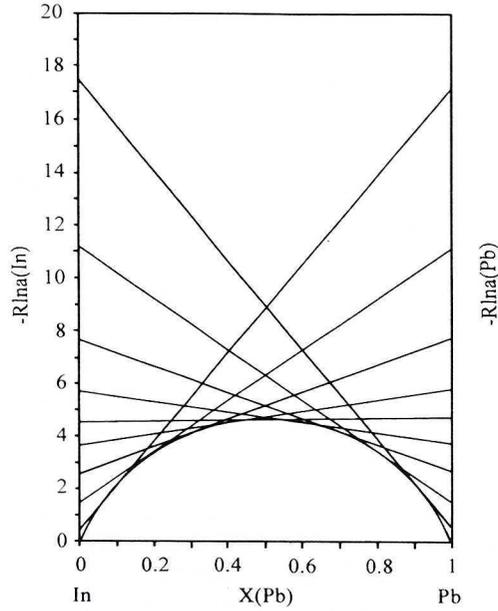
Fig. 4. Tangent construction on Planck potential curve

Thermodynamic values for system Pb and In determined by DTA method

a) 673 K

|  | $\gamma(Pb)$ | $a(Pb)$ | $\gamma(In)$ | $a(In)$ | $G^{XS}(Pb)$ | $G^{XS}(In)$ | $\Delta G^{XS}$ | $G^M(Pb)$ | $G^M(In)$ | $\Delta G^M$ |
|---|---|---|---|---|---|---|---|---|---|---|
| U1 | 1.3579 | 0.0607 | 1.0122 | 0.967 | 1711.82 | 68.07 | 141.5 | −15677 | −187.7 | −880 |
| U2 | 1.36 | 0.136 | 1.0466 | 0.942 | 1720.47 | 254.84 | 401.4 | −11163 | −334.3 | −1417 |
| U3 | 1.357 | 0.181 | 1.0385 | 0.900 | 1708.11 | 211.376 | 410.8 | −9563 | −588.9 | −1785 |
| U4 | 1.365 | 0.273 | 1.0487 | 0.839 | 1741.0 | 266.33 | 561.2 | −7264 | −982.2 | −2238 |
| U5 | 1.3658 | 0.305 | 1.066 | 0.828 | 1744.57 | 357.61 | 667.3 | −6644 | −1056 | −2303 |
| U6 | 1.272 | 0.509 | 1.0866 | 0.652 | 1348.38 | 464.71 | 818.1 | −3778 | −2393 | −2947 |
| U7 | 1.15 | 0.575 | 1.178 | 0.589 | 782.01 | 916.614 | 849.3 | −3096 | −2961.7 | −3029 |
| U8 | 1.08 | 0.648 | 1.29 | 0.516 | 430.62 | 1424.8 | 828.2 | −2427 | −3702.2 | −2937 |
| U9 | 1.043 | 0.835 | 1.38 | 0.276 | 239.32 | 1802.1 | 551.8 | −1008 | −7203 | −2247 |
| U10 | 1.048 | 0.944 | 1.32 | 0.132 | 266.59 | 1553.43 | 395.2 | −322 | −11330 | −1423 |

a) 773 K

|  | $\gamma$(Pb) | $a$(Pb) | $\gamma$(In) | $a$(In) | $G^{XS}$(Pb) | $G^{XS}$(In) | $\Delta G^{XS}$ | $G^{M}$(Pb) | $G^{M}$(In) | $\Delta G^{M}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| U1 | 1.2304 | 0.055 | 1.0045 | 0.957 | 1332.6 | 28.863 | 87.14 | $-18640$ | $-265.0$ | $-1086$ |
| U2 | 1.24 | 0.124 | 1.0465 | 0.941 | 1382.4 | 292.44 | 401.4 | $-13415$ | $-384.6$ | $-1687$ |
| U3 | 1.2378 | 0.165 | 1.0176 | 0.882 | 1371.09 | 112.46 | 280.2 | $-11579$ | $-806$ | $-2242$ |
| U4 | 1.315 | 0.263 | 1.0312 | 0.825 | 1759.8 | 197.76 | 510.1 | $-8583$ | $-1236$ | $-2705$ |
| U5 | 1.3166 | 0.294 | 1.0369 | 0.805 | 1767.4 | 233.19 | 575.8 | $-7867$ | $-1390$ | $-2837$ |
| U6 | 1.2425 | 0.497 | 1.0683 | 0.641 | 1395.4 | 424.8 | 813.0 | $-4493$ | $-2858$ | $-3512$ |
| U7 | 1.144 | 0.572 | 1.15 | 0.575 | 864.59 | 898.21 | 881.4 | $-3590$ | $-3556$ | $-3573$ |
| U8 | 1.065 | 0.639 | 1.25 | 0.5 | 404.72 | 1434 | 816.4 | $-2878$ | $-4454$ | $-3508$ |
| U9 | 1.0375 | 0.83 | 1.295 | 0.259 | 236.59 | 1661.3 | 521.5 | $-1197$ | $-8682$ | $-2694$ |
| U10 | 1.0466 | 0.942 | 1.23 | 0.123 | 293.126 | 1330.4 | 396.8 | $-383.9$ | $-8682$ | $-1692$ |

b) 873 K

|  | $\gamma$(Pb) | $a$(Pb) | $\gamma$(In) | $a$(In) | $G^{XS}$(Pb) | $G^{XS}$(In) | $\Delta G^{XS}$ | $G^{M}$(Pb) | $G^{M}$(In) | $\Delta G^{M}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| U1 | 1.1856 | 0.053 | 1.0031 | 0.958 | 1236 | 22.75 | 76.998 | $-21320$ | $-309$ | $-1248$ |
| U2 | 1.19 | 0.119 | 1.0422 | 0.938 | 1262 | 300.1 | 396.4 | $-15449$ | $-464$ | $-1963$ |
| U3 | 1.1852 | 0.158 | 1.0141 | 0.879 | 1233 | 102.2 | 253.1 | $-13392$ | $-936$ | $-2596$ |
| U4 | 1.245 | 0.249 | 1.031 | 0.825 | 1590.5 | 223.34 | 496.7 | $-10091$ | $-1396$ | $-3135$ |
| U5 | 1.244 | 0.278 | 1.0325 | 0.8022 | 1590.2 | 232.6 | 535.8 | $-9291$ | $-1601$ | $-3318$ |
| U6 | 1.2125 | 0.485 | 1.0616 | 0.637 | 1398 | 434.3 | 820 | $-5252$ | $-3273$ | $-4064$ |
| U7 | 1.124 | 0.562 | 1.136 | 0.568 | 848.4 | 925.5 | 886.9 | $-4182$ | $-4105$ | $-4143$ |
| U8 | 1.045 | 0.627 | 1.2425 | 0.497 | 319.4 | 1575 | 822.05 | $-3388$ | $-5074$ | $-4062$ |
| U9 | 1.032 | 0.826 | 1.25 | 0.25 | 232.1 | 1619 | 509.6 | $-1387$ | $-10061$ | $-3122$ |
| U10 | 1.044 | 0.939 | 1.17 | 0.117 | 314 | 1139 | 396.6 | $-450.6$ | $-15572$ | $-1962$ |

c) 973 K

| | $\gamma(\mathrm{Pb})$ | $a(\mathrm{Pb})$ | $\gamma(\mathrm{In})$ | $a(\mathrm{In})$ | $G^{XS}(\mathrm{Pb})$ | $G^{XS}(\mathrm{In})$ | $\Delta G^{XS}$ | $G^{M}(\mathrm{Pb})$ | $G^{M}(\mathrm{In})$ | $\Delta G^{M}$ |
|----|------|------|--------|-------|------|------|-------|---------|---------|--------|
| U1 | 1.138 | 0.05 | 1.033 | 0.958 | 1050 | 24.5 | 70.39 | $-24089$ | $-345$ | $-1406$ |
| U2 | 1.1 | 0.11 | 1.0411 | 0.937 | 771 | 325 | 370.4 | $-17855$ | $-526$ | $-2259$ |
| U3 | 1.14 | 0.152 | 1.0038 | 0.87 | 1061 | 30.7 | 168.2 | $-15239$ | $-1126$ | $-3007$ |
| U4 | 1.19 | 0.238 | 1.0275 | 0.822 | 1407 | 219 | 457 | $-11612$ | $-1585$ | $-3591$ |
| U5 | 1.186 | 0.265 | 1.0287 | 0.799 | 1385 | 228 | 487 | $-10743$ | $-1815$ | $-3808$ |
| U6 | 1.175 | 0.47 | 1.0583 | 0.635 | 1304 | 458 | 797 | $-6107$ | $-3673$ | $-4647$ |
| U7 | 1.102 | 0.551 | 1.12 | 0.56 | 785 | 916 | 851 | $-4821$ | $-4690$ | $-4755$ |
| U8 | 1.035 | 0.621 | 1.2175 | 0.487 | 278 | 1582 | 803 | $-3854$ | $-5820$ | $-4640$ |
| U9 | 1.025 | 0.82 | 1.215 | 0.243 | 199 | 1575 | 474.8 | $-1605$ | $-11444$ | $-3573$ |
| U10 | 1.042 | 0.938 | 1.15 | 0.115 | 334 | 1130 | 314.1 | $-517$ | $-17496$ | $-2215$ |
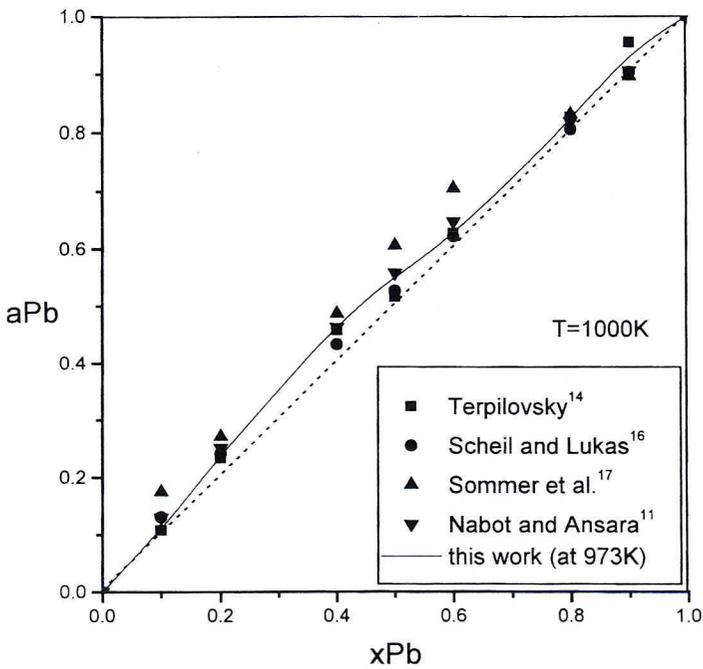


a)
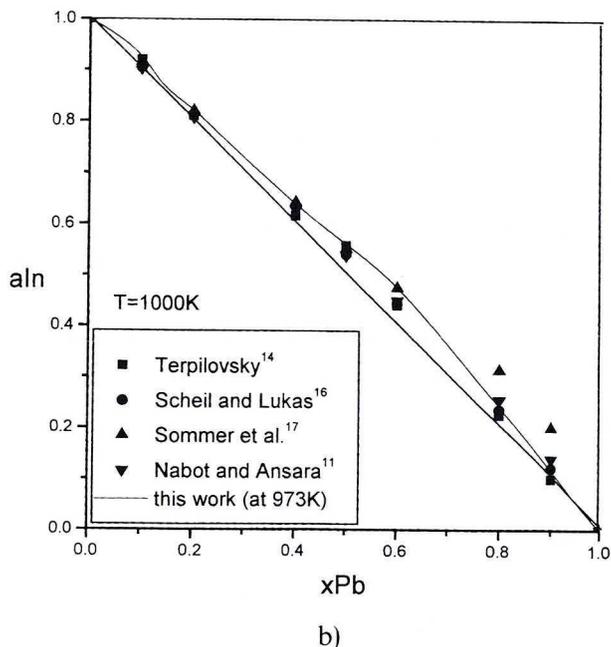
Fig. 5. Dependencies of activities vs. composition for: a) Pb; b) In in comparison with literature data

Positive deviation from R a o u l t law, for both components in the Pb–In system, can be noticed at all investigated temperatures and indicates the weak interactions between lead and indium. This influences the positive values for partial and integral excess Gibbs energies. Also, the activity values decrease with temperature increase and become nearer to the line of ideal solution behaviour.

The comparative review of the experimentally obtained and literature data for the lead and indium activity values at the temperature 1000 K is shown in Fig. 5. A good agreement could be noticed.

## 4. Conclusions

Results of thermodynamic analysis of binary Pb–In system, determined by quantitative DTA method, are presented in this paper. Adequate calibration constants are determined and linear dependence of $gKs$ on composition is proved. Values for the enthalpy of mixing in liquid and solid state show agreement with literature data. The comparison between experimentally obtained activity values and literature data show relatively good agreement.

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