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The Ag–Bi–In system: enthalpy of formation

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Abstract

The Ag–Bi–In ternary alloys as lead-free solder candidates in electronic industry were studied. Using a high temperature microcalorimeter, the enthalpy of formation of this system was determined along six isoplethic sections ($x_{\mathrm{Bi}}/x_{\mathrm{In}} = 1/4$, 1/2, 1/1, 62/38, $x_{\mathrm{Ag}}/x_{\mathrm{Bi}} = 1/3$ and $x_{\mathrm{Ag}}/x_{\mathrm{In}} = 1/1$) in the temperature range of 809–911 K. A critical analysis of these results leads us to the following conclusion: the enthalpy of formation of the Ag–Bi–In liquid system ($\Delta_{\mathrm{mix}}H^{\circ}_{\mathrm{m(Ag-Bi-In)}} = f(x_{\mathrm{Ag}}, x_{\mathrm{Bi}})$) can be correctly represented by the Toop relation on the entire ternary molar fraction range.

Keywords: Silver–bismuth–indium system; Liquid alloys; Calorimetry; Enthalpy of formation

1. Introduction

Because of the toxic nature of lead, the use of this metal is restricted in many applications and especially in the production of solder joints. As an example, among the quantity of lead contained in a computer (about 2 g) only 4/5 are recovered, and remains are being thrown towards environment. So we cannot continue in this vein and we must find convenient lead-free solders. So, researches in the field of the lead-free solders are important and the elements which are possible candidates for solders in tin-base alloys are: Bi, In, Ag, Zn, Sb, etc.

These multi-component alloys must present a low acceptable melting point, a small melting range, a good wettability, good mechanical properties, a high driving force of formation for interface reaction with metallic substrate, small values of surface tension, etc. Moreover, some intermetallic filler particules (Cu_6Sn_5 for instance) can be added to these alloys to improve the mechanical properties of the solder and increase their resistance to the degradation in long term aging. Usually, the silver–indiun–tin mixtures (with also Cu, the brazes) are already of industrial importance.

Moreover, bismuth is one of the most interesting metals in the development of lead-free solders. Bi element, in low composition range, enhances wetting ability and increases creep and fatigue resistance [1]. But a complete knowledge of the physical and chemical properties of ternary, quaternary, etc. systems is not attainable by the only experimental way.

Nevertheless the knowledge of the thermodynamic properties of these binary, ternary, quaternary alloys that allow the corresponding phase diagrams to be calculated and the variations of physical properties to be predicted is very important. Consequently, a sys-

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tematic investigation of the thermodynamic properties of the *n*-low melting components alloys has been undertaken [2–4]. Previously, using a convenient galvanic cell, the activity of indium in the Ag–Bi–In system has been measured; this present study proposes the integral molar enthalpy of formation obtained by calorimetry and an analytical relation for the $\Delta_{\text{mix}}H^{\circ}_{\text{m(Ag–Bi–In)}} = f(x_{\text{Ag}}, x_{\text{Bi}})$ function.

2. Bibliographic surview

In the following the two kinds of thermodynamic information (phase diagram and enthalpy of formation) concerning the limiting binary alloys and the ternary system have been recalled.

2.1. The Ag–Bi system

2.1.1. Phase diagram

The equilibrium phase diagram [5] exhibits a eutectic point ($T_{\text{eut}} = 535.7$ K, $x_{\text{Bi}} = 0.953$) shifted on the Bi-rich side (Fig. 1 from [6]). In solid state, the maximum of the solubility of bismuth in silver is located at about 773 K ($x_{\text{Bi}} = 0.028$). The small solid solubility of silver in bismuth seems unknown.

2.1.2. Enthalpy of formation

Several experimental results of the enthalpy of formation have been published. In 1993, a very complete critical compilation of the thermodynamic data was proposed by Karakaya and Thomson [7]. Moreover, on the one hand, Kameda and Yamaguchi [8] from EMF measurements with a galvanic cell using a zirconia solid electrolyte ($880 < T(\text{K}) < 1065$), and on the other hand, Hassam et al. [9] from direct high temperature calorimetric measurements, have obtained new thermodynamic data.

Hassam found a small exothermic heat of formation in the very rich silver region. These results—obtained at 878 K and retained for this study—can be represented by the equation:

$$\Delta_{\text{mix}}H^{\circ}_{\text{m}}\ (\text{kJ mol}^{-1}) = x_{\text{Bi}}(1 - x_{\text{Bi}})(-6.95_6 + 41.13_7 x_{\text{Bi}} - 30.10_9 x^2_{\text{Bi}} + 7.91_2 x^3_{\text{Bi}}) \quad (1)$$

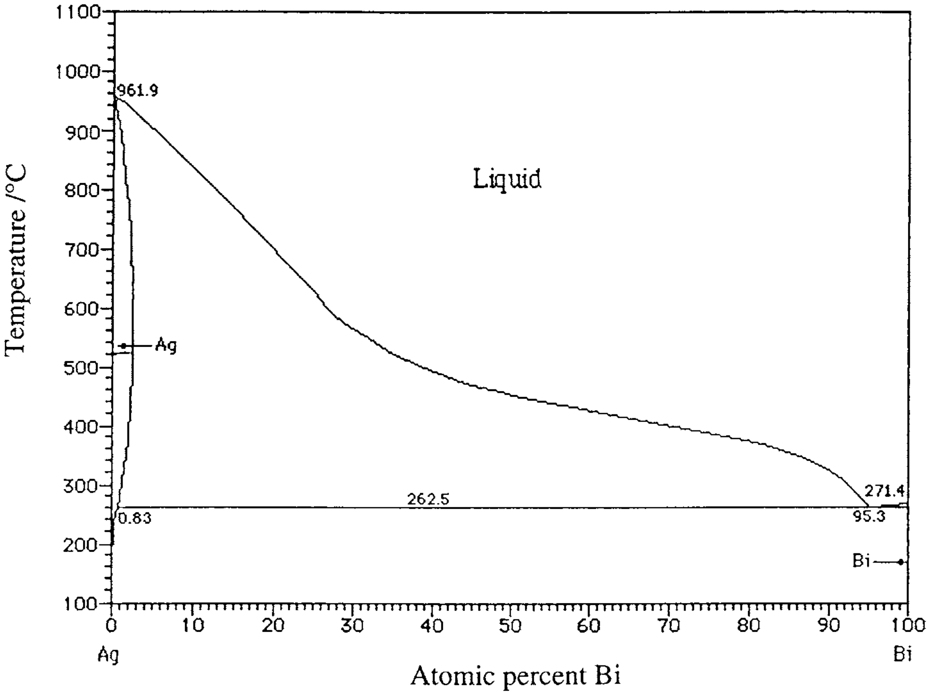


Fig. 1. The equilibrium phase diagram (in °C and at.%) of the binary Ag–Bi system (from Ref. [6]).

In 1994, Kattner and Boettinger [10] in order to predict the thermodynamic properties and the phase diagram of the Ag–Bi–Sn system have analyzed and compared all the experimental data. Then they calculated values of the enthalpy and Gibbs free energy of the Ag–Bi system. Experimental and predicted phase diagrams are in reasonable agreement.

2.2. The Ag–In system

2.2.1. Phase diagram

The equilibrium phase diagram [5] exhibit four definite compounds which melt incongruently and a eutectic point near the pure indium metal ($x_{\text{In}} = 0.96$ with $T_{\text{eut}} = 417$ K). The solid solubility of indium in silver is large ($x_{\text{In}} = 0.20$ at $T = 700$ K) whereas the solubility of silver in indium is almost zero (Fig. 2 from [6]).

2.2.2. Enthalpy of formation

Kleppa [11] at 723 K, Orr and Hultgren [12] at 317 K, Béjà and Laffitte [13] at 773 and 1028 K, then Castanet et al. [14] at 743 K and 1280 K have measured the enthalpy of formation by direct calorimetry. From these experimental results, Hultgren et al. [5] proposed the following equation of the enthalpy of mixing:

$$\Delta_{\text{mix}}H^{\circ}_{\text{m}}\ (\text{kJ mol}^{-1}) = x_{\text{In}}(1 - x_{\text{In}})(-14.74_6 - 76.50_2 x_{\text{In}} + 199.67_0 x_{\text{In}}^2 - 114.98_0 x_{\text{In}}^3) \qquad (2)$$

Other thermodynamic measurements were also performed by Guojun et al. [15] (by vapor pressure measurements), Kameda et al. [16] (by potentiometry). Using the ideal associated solution model, Wasai and Mukai [17] have calculated the excess functions of formation of this binary system.

2.3. The Bi–In system

2.3.1. Phase diagram

Three compounds (Fig. 3 from [6]): BiIn (melting point at 383.2 K), Bi_3In_5 (peritectic at 362 K) et $BiIn_2$

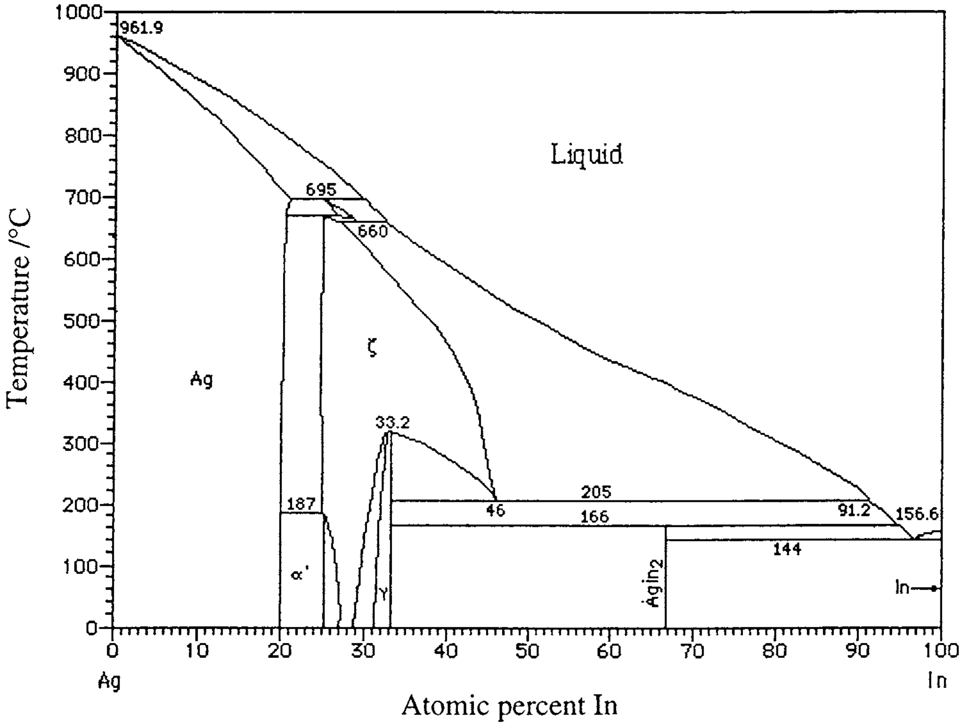


Fig. 2. The equilibrium phase diagram (in °C and at.%) of the binary Ag–In system (from Ref. [6]).

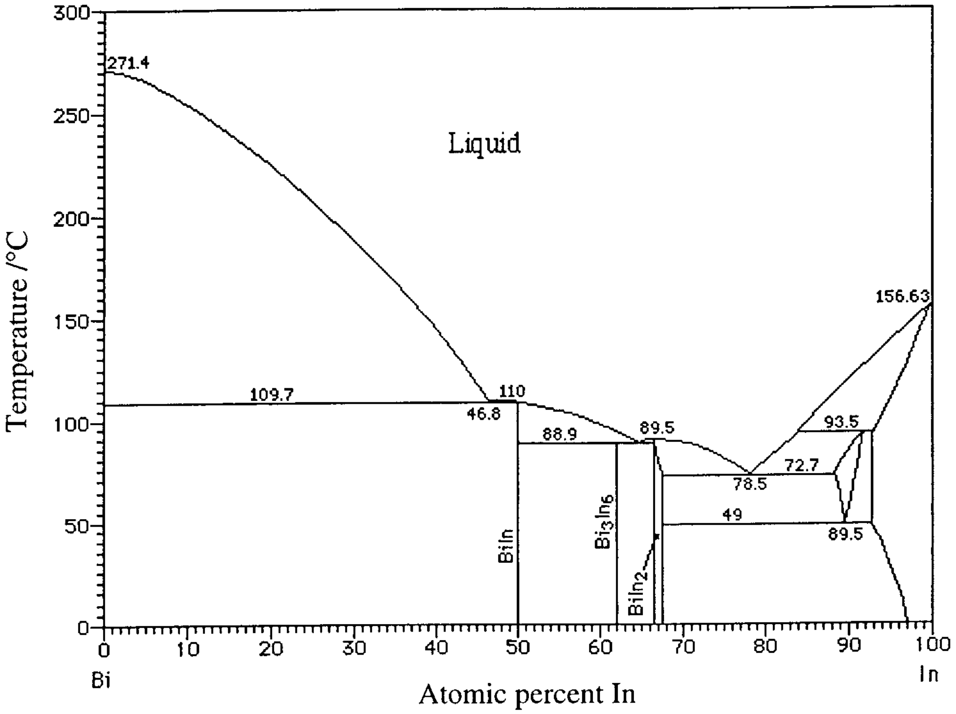


Fig. 3. The equilibrium phase diagram (in °C and at.%) of the binary Bi–In system (from Ref. [6]).

(melting point at 362.6 K) have been found as well as the ϵ phase located between 322 K and 367 K in the molar fraction range $0.88 < x_{\mathrm{Bi}} < 0.92$. The coordinates of the two eutectic points have been precised by Charles et al. [18]: $x_{\mathrm{Bi}} = 0.785$ at $T_{\mathrm{eut}} = 345.8$ K and $x_{\mathrm{Bi}} = 0.468$ at $T_{\mathrm{eut}} = 382.8$ K.

In 1988, using the CALPHAD method, Chevalier [19] has proposed a set of coherent thermodynamic data for this system. The coordinates of the invariant points are in good agreement with the results given in Ref. [18].

2.3.2. Enthalpy of formation

Obtained from calorimetric measurements, the enthalpies of formation of the Bi–In liquid system have been compiled by Hultgren et al. [5]. They proposed the following relation (in kJ mol^{-1}) retained for this work:

$$\begin{aligned}\Delta_{\mathrm{mix}}H^{\circ}_{\mathrm{m}}\ (\mathrm{kJ\,mol^{-1}}) &= x_{\mathrm{In}}(1-x_{\mathrm{In}})(-6.12_6 - 2.39_2x_{\mathrm{In}} \\ &\quad - 16.74_3x_{\mathrm{In}}^2 + 14.60_9x_{\mathrm{In}}^3)\end{aligned}$$

In 1989, the values of activities measured by Kameda [20] (EMF technique) are in agreement with those already published [5]. On the contrary, the data of Bichara et al. [21] of the limiting molar partial enthalpy of indium in bismuth seems significantly different.

2.4. The Ag–Bi–In system

The phase diagram of this system is not available. Using potentiometric cell with zirconia electrolyte, Kameda and Yamaguchi [22] and Vassiliev et al. [4] measured the activities of indium in liquid Ag–Bi–In alloys in the temperature range 896–1297 K along the sections $x_{\mathrm{Bi}}/x_{\mathrm{Ag}} = 4/1$, 1/1 and 1/4. From results obtained with 15 different ternary alloys, the isoactivity curves at 1100 and 1200 K have been proposed.

Moreover several partial results can be found in special papers dealing with the lead-free tin alloy solders but, generally, these information mainly concern the Sn-rich alloys. Nevertheless the enthalpy of formation of this liquid alloy is not available in the entire concentration range.

3. Experimental

3.1. High temperature calorimetry

With a Calvet high temperature microcalorimeter—described elsewhere [23,24]—the determination of the enthalpy of formation of the Ag–In and Ag–Bi–In liquid systems have been performed at 809, 896 and 911 K using the well-known direct drop method [25]. The calorimeter cell was a quartz tube (600 mm height and 16 mm external diameter). At the lower end, the cell was shaped to fit the thermopile dimension. In the upper part of the quartz cell, a special device allows the metal samples to be introduced and the constant purified argon flow to pass over the crucible.

The alloying process was performed in pure graphite (or alumina) crucibles fitting tightly with the quartz tube of the cell.

At first, before starting a series of measurements, the graphite crucible was charged with a fixed amount of indium (to synthesize the Ag–In binary alloy) or of a binary alloy (Ag–Bi or Ag–In or Bi–In to synthesize ternary alloys) and introduced in the quartz calorimetric cell. When the experimental temperature was stabilized, small pieces of metal (Ag or Bi or In) were added consecutively into the bath.

The metals used were silver (wire), bismuth (ingot), indium (ingot) with nominal purities of 99.999 wt.%. To prepare the samples (with a mass between 20 and 60 mg), metals were rinsed with pure acetone (high purity), dried and cut in small pieces. All experimental runs are performed under high purity argon (Argon N56 from Air Liquid).

The calorimeter was calibrated at the end of each measurement series by dropping known amounts of α-alumina (purchased from NIST [26]) from ambient temperature into the experimental cell at working temperature. The relative enthalpies of α-alumina pieces were calculated by using the $C_p^\circ = f(T)$ data published by NIST.

Molar enthalpies of pure added metal (Ag, Bi and In) were calculated from [27] assuming that the molar heat capacity of the liquid and the supercooled liquid phase have the same value and that the enthalpy of melting is not temperature dependent.

Taking into account the shape of the liquidus lines of the two binary limiting systems (Figs. 1 and 2) Ag–Bi and Ag–In, we can assume that the domain of the liquid monophase Ag–Bi–In will be large enough to measure, by direct calorimetry, the enthalpy of formation in a large molar fraction range and then to obtain by extrapolation this function at all the ternary compositions.

In the experimental temperature range ($809 < T(\mathrm{K}) < 911$), the vapor pressure of silver, bismuth and indium are sufficiently low to assume a negligible loss of metal by evaporation (at 800 K $p_{\mathrm{Ag}} = 1.4 \times 10^{-7}$ Pa, $p_{\mathrm{Bi}} = 4.43 \times 10^{-3}$ Pa, $p_{\mathrm{In}} = 8.0 \times 10^{-6}$ Pa) [28]. The difference between the mass of the final alloy and the sum of the masses of the metals charged in the cell was always less than 1%. The error in the enthalpies of formation of a ternary liquid alloy was estimated at about ±4%. The experimental temperature was obtained using a Pt/Pt–Rh 10 wt.% thermocouple with an accuracy of ±2 K.

4. Results

The enthalpy of formation has been measured along six sections (Fig. 4):

- $x_{\mathrm{Bi}}/x_{\mathrm{In}} = 1/4$ with $0 < x_{\mathrm{Ag}} < 0.45$ at 896 K;
- $x_{\mathrm{Bi}}/x_{\mathrm{In}} = 1/2$ with $0 < x_{\mathrm{Ag}} < 0.55$ at 809 K;
- $x_{\mathrm{Bi}}/x_{\mathrm{In}} = 1/1$ with $0 < x_{\mathrm{Ag}} < 0.41$ at 809 and 911 K;

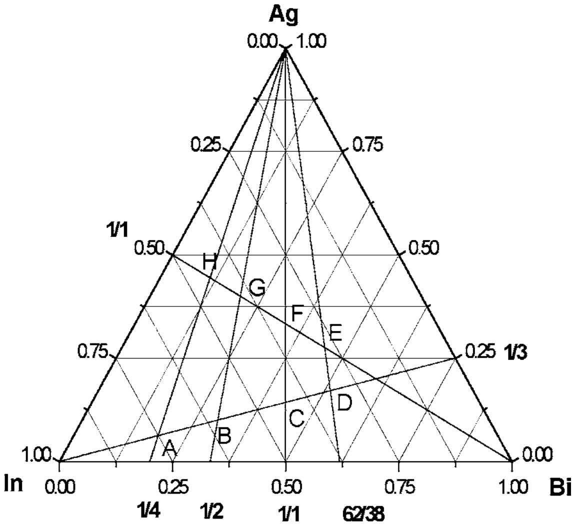


Fig. 4. Sections along which the experimental determinations were performed.

Table 1

Enthalpies of formation of Ag–Bi–In liquid alloys along the section: (a) $x_{\mathrm{Bi}}/x_{\mathrm{In}} = 1/4$ at 896 K; (b) $x_{\mathrm{Bi}}/x_{\mathrm{In}} = 1/2$ at 809 K; (c) $x_{\mathrm{Bi}}/x_{\mathrm{In}} = 1/1$ at 809 and 911 K; (d) $x_{\mathrm{Bi}}/x_{\mathrm{In}} = 62/38$ at 809 and 911 K; (e) $x_{\mathrm{Ag}}/x_{\mathrm{In}} = 1/1$ at 896 K; (f) $x_{\mathrm{Ag}}/x_{\mathrm{Bi}} = 1/3$ at 896 K

x_{Ag}	x_{Bi}	x_{In}	$-\Delta_{\mathrm{mix}}H^{\circ}_{\mathrm{m}}$ (calculated, J mol^{-1})	$-\Delta_{\mathrm{mix}}H^{\circ}_{\mathrm{m}}$ (experimental, J mol^{-1})	Deviation (%)
(a) $x_{\mathrm{Bi}}/x_{\mathrm{In}} = 1/4$ at 896 K					
0.0000	0.200	0.800	1192	1180	−1.0
0.0651	0.187	0.748	1177	1158	−1.7
0.1477	0.170	0.682	1199	1181	−1.5
0.2193	0.156	0.625	1389	1349	−2.9
0.2817	0.144	0.575	1714	1648	−4.0
0.3433	0.131	0.525	2157	2020	−6.5
0.3964	0.121	0.483	2597	2341	−10.4
0.4465	0.111	0.443	3021	2715	−10.7
0.0000	0.200	0.800	1192	1180	−1.0
0.0604	0.188	0.752	1180	1146	−2.9
0.1336	0.173	0.693	1183	1071	−9.9
0.2045	0.159	0.636	1334	1204	−10.2
0.2658	0.147	0.587	1618	1450	−11.0
0.3202	0.136	0.544	1980	1758	−11.9
0.3736	0.125	0.501	2404	2125	−12.3
0.4194	0.116	0.464	2793	2508	−10.8
(b) $x_{\mathrm{Bi}}/x_{\mathrm{In}} = 1/2$ at 809 K					
0.0000	0.333	0.667	1699	1736	2.2
0.1344	0.289	0.577	1298	1224	−5.8
0.2388	0.254	0.507	1323	1272	−4.0
0.3356	0.221	0.443	1709	1601	−6.5
0.3954	0.202	0.403	2070	1931	−7.0
0.0000	0.333	0.667	1699	1736	2.2
0.04655	0.318	0.636	1543	1482	−4.0
0.1242	0.292	0.584	1317	1250	−5.2
0.1964	0.268	0.536	1262	1210	−4.2
0.2612	0.246	0.493	1384	1306	−5.8
(c) $x_{\mathrm{Bi}}/x_{\mathrm{In}} = 1/1$ at 809 and 911 K					
0.0000	0.500	0.500	1822	1828	0.3
0.0495	0.475	0.475	1507	1435	−4.9
0.1069	0.447	0.447	1182	1097	−7.5
0.1572	0.421	0.421	974	901	−7.8
0.2021	0.399	0.399	867	814	−6.3
0.2487	0.376	0.376	839	768	−8.8
0.2865	0.357	0.357	877	801	−9.1
0.3212	0.339	0.339	956	879	−8.4
0.0000	0.500	0.500	1822	1828	0.3
0.0822	0.459	0.459	1313	1219	−7.4
0.1578	0.421	0.421	972	886	−9.3
0.2264	0.387	0.387	841	766	−9.4
0.2860	0.357	0.357	876	795	−9.7
0.3387	0.331	0.331	1010	918	−9.5
0.3855	0.307	0.307	1192	1089	−9.0
0.4265	0.287	0.287	1383	1275	−8.2
(d) $x_{\mathrm{Bi}}/x_{\mathrm{In}} = 62/38$ at 809 and 911 K					
0.000	0.618	0.382	1616	1638	1.4
0.137	0.533	0.330	654	650	−0.7
0.247	0.466	0.288	314	326	3.8

Table 1 (*Continued*)

x_{Ag}	x_{Bi}	x_{In}	$-\Delta_{\mathrm{mix}}H^{\circ}_{\mathrm{m}}$ (calculated, J mol^{-1})	$-\Delta_{\mathrm{mix}}H^{\circ}_{\mathrm{m}}$ (experimental, J mol^{-1})	Deviation (%)
0.332	0.413	0.255	360	385	6.7
0.401	0.370	0.229	555	598	7.4
0.458	0.335	0.207	790	1289	48.0[a]
0.503	0.307	0.190	992	2681	91.9[a]
0.547	0.280	0.173	1185	3396	96.5[a]
0.589	0.254	0.157	1352	4045	99.8[a]
0.000	0.618	0.382	1615	1638	1.4
0.133	0.536	0.331	675	701	3.8
0.240	0.470	0.290	421	340	5.6
0.328	0.415	0.257	352	383	8.3
0.398	0.372	0.230	547	591	7.7
(e) $x_{\mathrm{Ag}}/x_{\mathrm{Bi}} = 1/1$ at 896 K					
0.500	0.000	0.500	4363	4450	2.0
0.476	0.048	0.476	3735	3717	−0.5
0.440	0.120	0.440	2907	2617	−10.5
0.408	0.184	0.408	2253	2003	−11.8
0.380	0.240	0.380	1736	1519	−13.3
0.355	0.290	0.355	1319	1142	−14.4
0.333	0.335	0.333	981	845	−14.8
0.500	0.000	0.500	4363	4450	2.0
0.475	0.050	0.475	3711	3723	0.3
0.445	0.111	0.445	3005	2997	−0.3
0.418	0.165	0.418	2440	2385	−2.3
0.392	0.217	0.392	1942	1866	−4.0
0.368	0.265	0.368	1522	1462	−4.0
0.345	0.311	0.345	1374	1083	−6.5
(f) $x_{\mathrm{Ag}}/x_{\mathrm{Bi}} = 1/3$ at 896 K					
0.250	0.750	0.000	−1931	−1930	0.0
0.212	0.635	0.153	−585	−550	−6.2
0.175	0.526	0.299	398	367	−8.2
0.148	0.443	0.410	952	921	−3.3
0.127	0.380	0.493	1225	1168	−4.8
0.110	0.329	0.562	1348	1287	−4.7
0.096	0.288	0.616	1375	1296	−5.9
0.250	0.750	0.000	−1931	−1930	0.0
0.200	0.601	0.199	−253	−241	−4.7
0.164	0.492	0.344	646	599	−7.6
0.136	0.409	0.455	1117	1058	−5.4
0.115	0.345	0.540	1320	1254	−5.1
0.100	0.299	0.601	1374	1281	−7.0

[a] Values obtained in the two phases region.

- $x_{\mathrm{Bi}}/x_{\mathrm{In}} = 62/38$ with $0 < x_{\mathrm{Ag}} < 0.59$ at 809 and 911 K;
- $x_{\mathrm{Ag}}/x_{\mathrm{In}} = 1/1$ with $0 < x_{\mathrm{Bi}} < 0.34$ at 896 K;
- $x_{\mathrm{Ag}}/x_{\mathrm{Bi}} = 1/3$ with $0 < x_{\mathrm{In}} < 0.62$ at 896K.

Calorimetric measurements (in J mol^{-1}) are reported in Table 1a–f and Fig. 5a–f. In this temperature range the enthalpy of mixing seems to be no temperature dependent.

In Table 2 are gathered the coordinates of the intersections (A, B, C, D, E, F, G, H) of the sections and the experimental values of the enthalpy of formation obtained independently (for example, at the point C, the enthalpy of mixing has been obtained either by

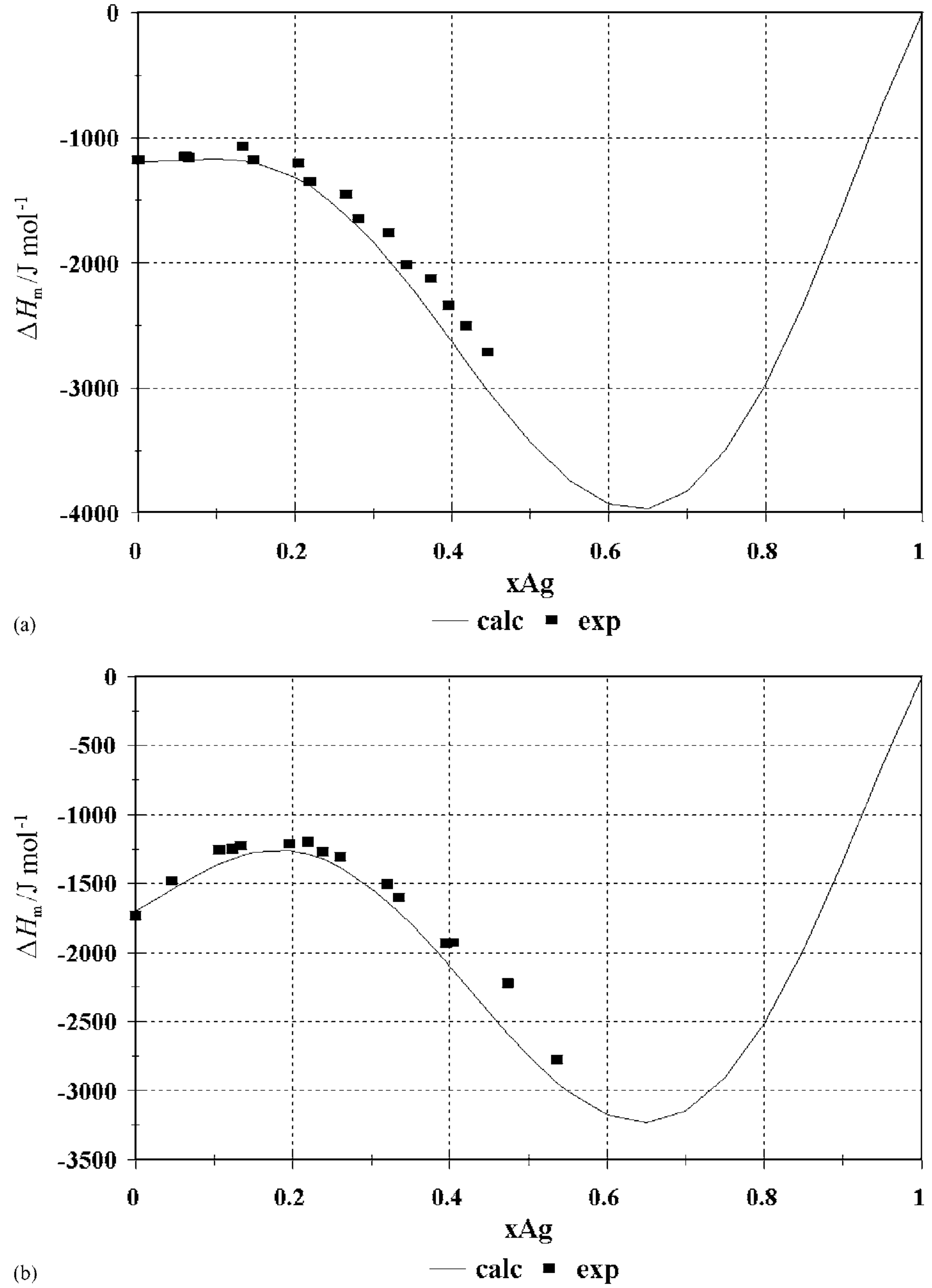


Fig. 5. (a) Enthalpy of formation (in J mol^{-1}) of the Ag–Bi–In liquid alloys along the section $x_{Bi}/x_{In} = 1/4$ at 896 K. (■) Experimental results; (—) obtained using the Toop relation. (b) Enthalpy of formation (in J mol^{-1}) of Ag–Bi–In liquid alloys along the section $x_{Bi}/x_{In} = 1/2$ at 809 K. (■) Experimental results; (—) obtained using the Toop relation. (c) Enthalpy of formation (in J mol^{-1}) of Ag–Bi–In liquid alloys along the section $x_{Bi}/x_{In} = 1/1$ at 809 and 911 K. (■) Experimental results; (—) obtained using the Toop relation. (d) Enthalpy of formation (in J mol^{-1}) of Ag–Bi–In liquid alloys along the section $x_{Bi}/x_{In} = 62/38$ at 809 K and 911 K. (■) Experimental results; (—) obtained using the Toop relation (⧗) liquidus point. (e) Enthalpy of formation (in J mol^{-1}) of Ag–Bi–In liquid alloys along the section $x_{Ag}/x_{In} = 1/1$ at 896 K. (■) Experimental results; (—) obtained using the Toop relation. (f) Enthalpy of formation (in J mol^{-1}) of Ag–Bi–In liquid alloys along the section $x_{Ag}/x_{Bi} = 1/3$ at 896 K. (■) Experimental results; (—) obtained using the Toop relation.

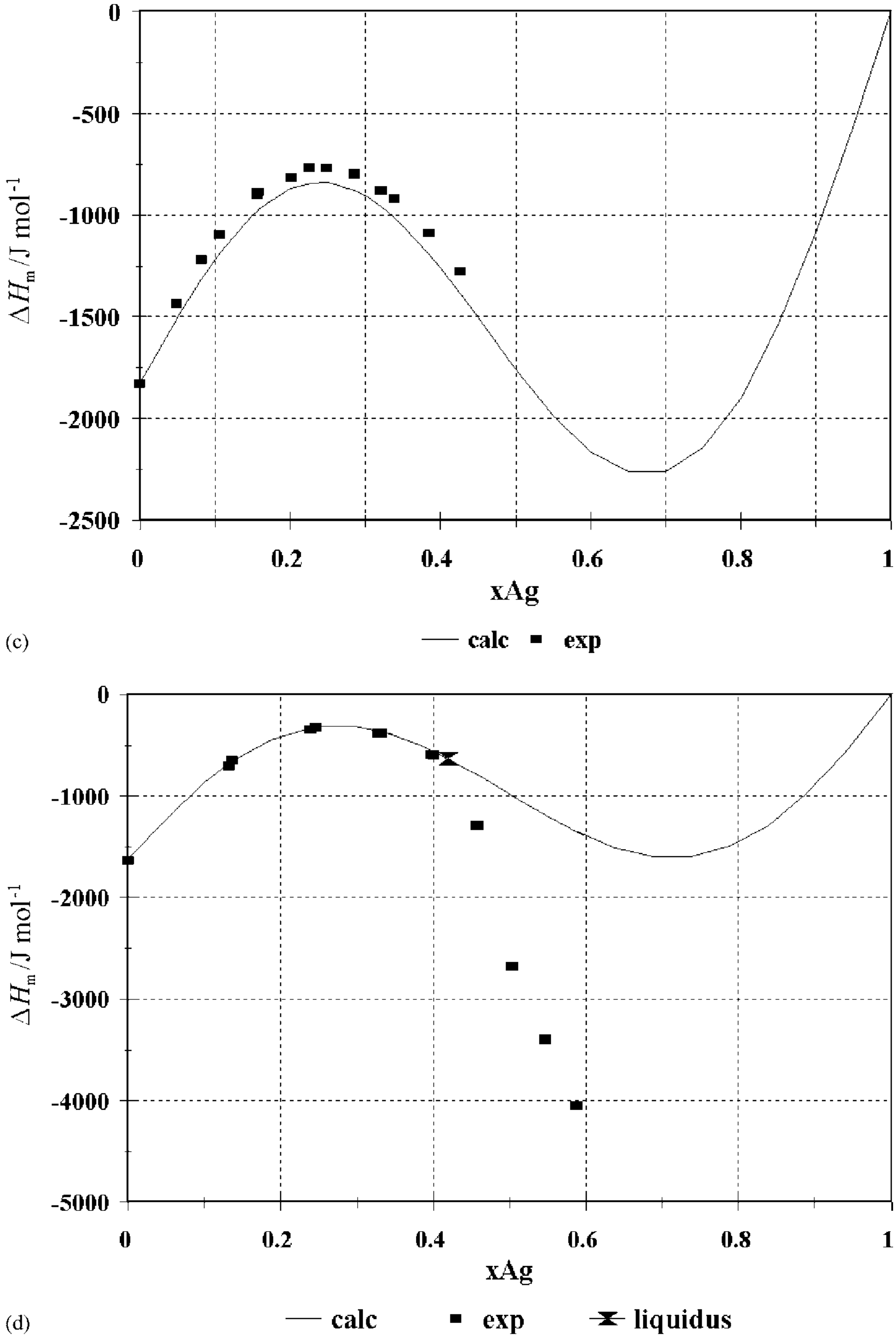
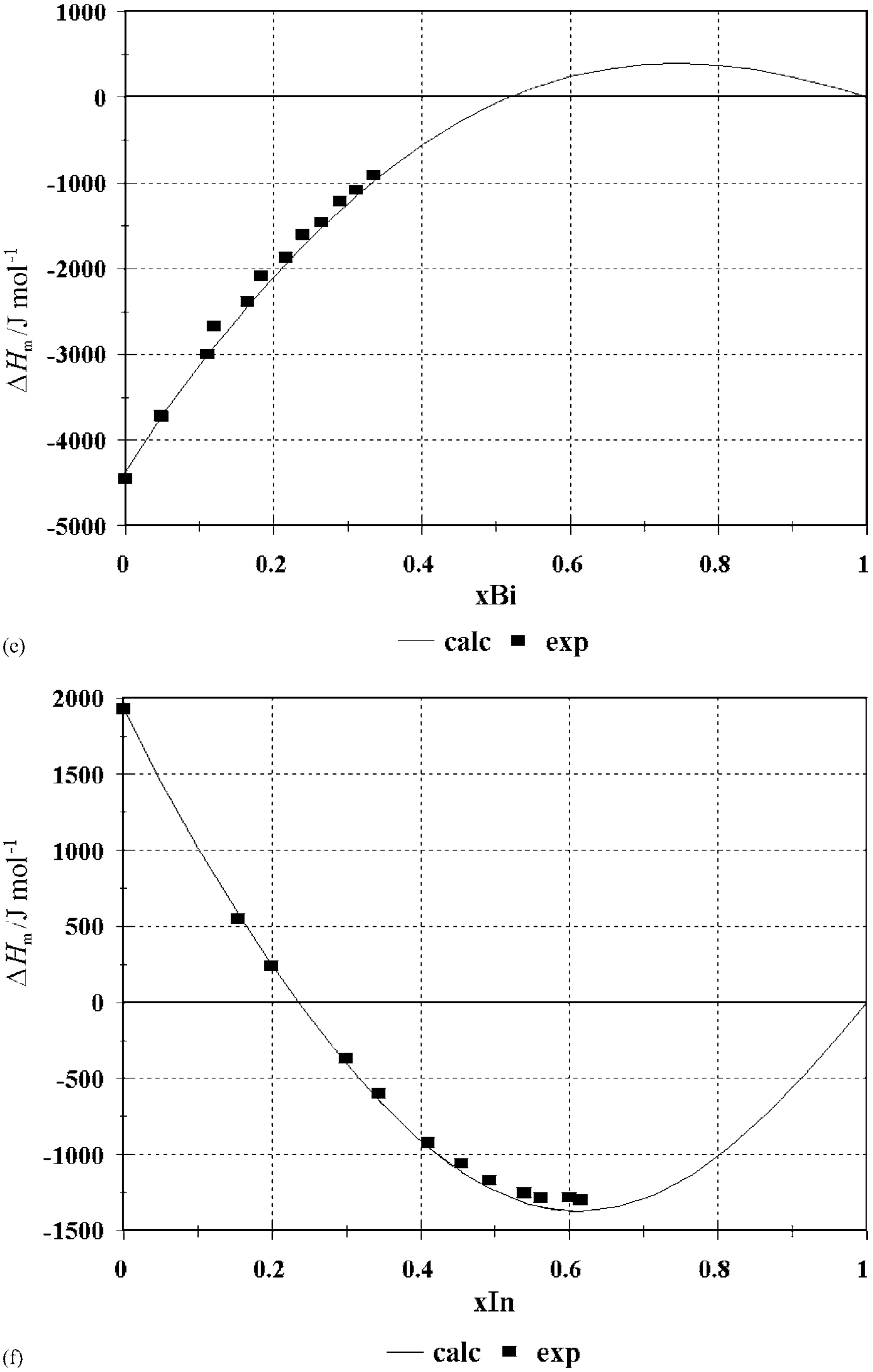


Fig. 5. (*Continued*).



(c)

(f)

Fig. 5. (*Continued*).

Table 2
Coordinates of the intersections of the investigated sections and the enthalpy of formation corresponding values

Points	x_{Ag}	x_{Bi}	x_{In}	$-\Delta_{mix}H^\circ_m$ (J mol^{-1})	$-\Delta_{mix}H^\circ_m$ (J mol^{-1})
A	0.06_3	0.18_8	0.75_0	1200[a] on $x_{Ag}/x_{Bi} = 1/3$	1160 on $x_{Bi}/x_{In} = 1/4$
B	0.10_0	0.30_0	0.60_0	1700[a] on $x_{Ag}/x_{Bi} = 1/3$	1320 on $x_{Bi}/x_{In} = 1/2$
C	0.14_3	0.42_9	0.42_9	960 on $x_{Ag}/x_{Bi} = 1/3$	1030 on $x_{Bi}/x_{In} = 1/1$
D	0.17_1	0.51_4	0.31_5	450 on $x_{Ag}/x_{Bi} = 1/3$	500 on $x_{Bi}/x_{In} = 62/38$
E	0.27_5	0.44_9	0.27_5	300[a] on $x_{Ag}/x_{In} = 1/1$	350 on $x_{Bi}/x_{In} = 62/38$
F	0.33_3	0.33_3	0.33_3	850 on $x_{Ag}/x_{In} = 1/1$	915 on $x_{Bi}/x_{In} = 1/1$
G	0.40_0	0.20_0	0.40_0	1900 on $x_{Ag}/x_{In} = 1/1$	1925 on $x_{Bi}/x_{In} = 1/2$
H	0.44_4	0.11_1	0.44_4	2995 on $x_{Ag}/x_{In} = 1/1$	2715 on $x_{Bi}/x_{In} = 1/4$

[a] Obtained by extrapolation.

dropping Ag in $x_{Bi}/x_{In} = 1/1$ alloy or by dropping In in $x_{Ag}/x_{Bi} = 1/3$). The comparison of these investigated values of the enthalpy of formation is a criterion of the calorimetric results. Taking into account the experimental accuracy and the low level of the thermal effect of mixing, the results are in good agreement.

These experimental results have been compared to the corresponding data predicted by using the well-known analytical relations proposed by several authors [29–34] and the data of the binary limiting systems (Eqs. (1)–(3)). The best fit between calculated and experimental data is obtained with the following asymmetrical relation (Toop equation [34]):

$$\Delta_{mix}H^\circ_{m(ABC)} = \left[\frac{x_B}{1-x_A}\Delta_{mix}H^\circ_{m(AB)} + \frac{x_C}{1-x_A}\Delta_{mix}H^\circ_{m(AC)}\right]_{x_A} + (1-x_A)^2[\Delta_{mix}H^\circ_{m(BC)}]_{x_B/x_C}$$

with A, B and C corresponding to Ag, Bi and In, respectively.

Table 1a–f allows to compare experimental and calculated values.

Remark. The break point (⧗) in Fig. 5d corresponds to the appearance of a solid phase; it is a point of the liquidus surface of the Ag–Bi–In system.

5. Conclusion

A critical analysis of these results lead us to the following conclusion: the enthalpy of formation of the Ag–Bi–In liquid system $[\Delta_{mix}H^\circ_m = f(x_{Ag}, x_{Bi}, x_{In})]$ can be correctly represented by the Toop relation in the entire ternary molar fraction range. This relation will be used to calculate the other thermodynamic relation and the equilibrium phase diagram.

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