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Enthalpy of formation of the Bi + Cd + Ga + In + Sn + Zn liquid system

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Abstract

The molar enthalpy of formation of the Bi + Cd + Ga + In + Sn + Zn liquid system has been measured at 730 K by direct high-temperature calorimetry. Experimental results are compared with the values calculated using several equations (Kohler, Muggianu, Toop and Hoch–Arpshofen). Finally, an asymmetrical relation (the Toop relation) is proposed to describe the integral molar enthalpy of formation of this 6-component liquid system over the entire composition range.

Keywords: Enthalpy of formation; High temperature calorimetry; *n*-Component liquid alloys

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1. Introduction

The number of components in advanced metallic materials with specific applications has increased markedly over recent decades. Today, *n*-component alloys with $n > 4$ are not unusual. However, despite the experimental difficulties inherent with a large number of components, an accurate knowledge of the physical, mechanical and chemical properties is essential. Consequently, many studies have been carried out on *n*-component alloys to predict these properties. In the field of metallurgical thermochemistry, the excess functions (Gibbs energy, enthalpy, etc.) are of interest from both the fundamental and technological points of view.

The aim of the present research is to minimize the number of experiments required to propose a satisfactory analytical relationship for the molar function of formation of

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a 6-component liquid alloy. This research was made in the course of our thermodynamic study of liquid alloys [1–3]. Two points must be born in mind: (i) for the majority of the binary alloys containing metals in columns 12, 13, 14 and 15 of the IUPAC periodic table of the elements (from Zn to Bi), the thermodynamic properties have been studied extensively; (ii) a large number of relationships (or models) that predict the thermodynamic properties of *n*-component alloys is now available [4].

In this study, calorimetric measurements were performed at 730 K to obtain the enthalpy of formation of the Bi + Cd + Ga + In + Sn + Zn liquid alloy.

2. Bibliographic data

Knowledge of the thermodynamic properties of the fifteen binary sub-systems is required, both to organize the experiments and to predict the final enthalpy of formation.

2.1. Binary systems

For this work, only the data for the enthalpies of formation of binary liquid alloys have been retained. For each binary sub-system, this excess function has been determined using the relationship

$$\Delta_{\mathrm{mix}}H_m^{\ominus} = x_i(1-x_i)[A + Bx_i + Cx_i^2 + Dx_i^3] \tag{1}$$

where x_i is the mole fraction of the metal *i*.

Table 1 lists the values of the parameters (A, B, C and D in kJ mol^{-1}) for each system. The added element (*i*) and special features of the equilibrium phase diagram are indicated (eut., dem. and def. comp. mean eutectic point, liquid immiscibility gap and definite compound, respectively). Appended to Table 1 (column 8) are the references analysed [5–12]. From this review, it appears that none of these binary systems show strong interactions between their components. Only the Bi + In and In + Sn alloys exhibit definite compounds but their temperatures of fusion are less than those of the pure elements. So the existence of definite compounds with strong interatomic bonds in the *n*-component system seems improbable.

2.2. *n*-Component systems

To measure the enthalpies of formation of the Bi + Cd + Ga + In + Sn + Zn liquid alloy, the following two pathways have been used, at constant *T* and *P*

$$\mathrm{Bi + Cd + Ga + In + Zn(liq) + Sn(liq) \rightarrow Bi + Cd + Ga + In + Sn + Zn(liq)}$$

and

$$\mathrm{Cd + Ga + In + Sn + Zn(liq) + Bi(liq) \rightarrow Bi + Cd + Ga + In + Sn + Zn(liq)}$$

Table 1
Numerical coefficients (in kJ mol^{-1}) used in Eq. (1) to describe the integral molar enthalpy of formation of the limiting liquid binary systems. Columns 7 and 8 give the main characteristics of the equilibrium phase diagram (P.D.) of the limiting binary systems (with eut. = eutectic point, dem. = liquid immiscibility gap, def. comp. = definite compound) and the references, respectively

System	x_i	*A*	*B*	*C*	*D*	P.D.	Ref.
Bi + Cd	*x*Cd	2.697	2.016	−9.048	13.028	eut.	[5]
Bi + Ga	*x*Ga	1.710	40.883	−80.220	53.337	dem.	[6]
Bi + In	*x*In	2.392	−6.126	−16.740	14.609	def.comp.	[5]
Bi + Sn	*x*Sn	0.419				eut.	[5]
Bi + Zn	*x*Zn	13.691	5.284	7.006	0.395	dem.	[7]
Cd + Ga	*x*Ga	9.832	13.031	−38.850	31.309	dem.	[8]
Cd + In	*x*In	7.487	−5.777	5.969	−3.022	eut.	[5]
Cd + Sn	*x*Sn	9.882	−8.264	6.718	−1.687	eut.	[5]
Cd + Zn	*x*Zn	8.801	−1.881	1.883	0.420	eut.	[5]
Ga + In	*x*In	4.639	−1.139	14.742	0.066	eut.	[9]
Ga + Sn	*x*Sn	3.798	−0.754	0.133	0.109	eut.	[5]
Ga + Zn	*x*Zn	5.788	2.519	0.380	0.660	eut.	[10]
In + Sn	*x*Sn	−0.967	0.467	−0.078	−0.241	def.comp.	[5]
In + Zn	*x*Zn	10.827	5.604	−6.937	8.038	eut.	[5]
Sn + Zn	*x*Zn	8.058	14.979	−25.190	24.442	eut.	[11]

So the enthalpies of formation of the two quinary sub-systems from the Ga + Bi + Zn or Cd + Ga + Zn alloys were obtained by the following two pathways

$$\text{Ga} + \text{Bi} + \text{Zn(liq)}\,[\text{Refs. } 6, 12] + \text{Cd(liq)} \rightarrow \text{Ga} + \text{Bi} + \text{Cd} + \text{Zn(liq)}\,[\text{Ref. } 13]$$
$$+ \text{In(liq)} \rightarrow [\text{Ga} + \text{Bi} + \text{Cd} + \text{In} + \text{Zn(liq)}\,[\text{Ref. } 13]$$

and

$$\text{Cd} + \text{Ga} + \text{Zn(liq)}\,[\text{Ref.} 14] + \text{In(liq)} \rightarrow \text{Ga} + \text{Cd} + \text{In} + \text{Zn(liq)}\,[\text{Refs. } 2, 15]$$
$$+ \text{Sn(liq)} \rightarrow [\text{Ga} + \text{Cd} + \text{In} + \text{Sn} + \text{Zn(liq)}\,[\text{Refs. } 2, 15]$$

The values of the enthalpies of formation at the barycenter mole fractions ($x_1 = ... = x_i$) of each sub-system are listed in Table 2 and the references for these data are also reported.

3. Experimental procedure

All the enthalpies of mixing reported in this paper were measured using a high-temperature Calvet calorimeter. The principle of this calorimeter and its use have been the subject of several papers in the field of metallurgical thermochemistry [11, 16]. Therefore, only its main features will be discussed here. It can be operated up to 1300 K and all the main parts (the block and the three shields) are made of alumina. The block contains two thermopiles connected in opposition; each thermopile is made up of

Table 2
Values of the enthalpy of formation of the liquid quinary, quaternary and ternary systems at the barycenter

System (liq)	$\Delta_{\mathrm{mix}}H_m^{\ominus}/\mathrm{J\ mol^{-1}}$	T/K	Ref.
Cd + Ga + In + Sn + Zn	3150	730	[2, 15]
Bi + Cd + Ga + In + Zn	3170	730	[13]
Bi + Cd + Ga + Zn	3500	730	[13]
Cd + Ga + In + Zn	3096	730	[2, 15]
Bi + Ga + Zn	3535	873	[7, 11]
Cd + Ga + Zn	2882	730	[14]

496 thermocouples (Pt/Pt + Rh 10%). The calorimetric cells are cylindrical (80 mm high and 16 mm in diameter). The whole assembly is located within a vertical cylindrical furnace.

The peripheric equipment consists of a temperature regulator for the furnace, an automatic system for acquisition and treatment of calorimetric data, a potentiometric recorder for the measurements of experimental temperatures and thermal effects, and a gas-tight charging device.

Experiments were performed in graphite crucibles by dropping solid bismuth (or tin) into a liquid (Ga + Cd + In + Sn + Zn or Ga + Bi + Cd + In + Zn) alloy held at constant temperature (730 K). Small pieces of bismuth (or tin) were added consecutively. At the end of each series, up to seven additions of α-alumina pieces had been made in order to calibrate the calorimeter. (The α-alumina was from the National Institute of Standards and Technology, US Department of Commerce, Gaithersburg, Washington, USA.)

Metals of high purity (99.9995 wt%) employed in this study were from Koch Lights Company. A high purity graphite (from Carbone-Lorraine) was used to machine the crucibles. All experiments were performed under a pure argon atmosphere (Argon U from Air Liquide Company).

For the added metals (Bi and Sn) and for α-alumina, the molar heat capacities were taken from Hultgren et al. [17] and the National Institute of Standards and Technology, respectively.

At the end of each series, the final alloy was reweighed: the difference between the calculated and measured weights was than 0.1 mg, yielding errors of less than about 1% in the integral enthalpies of formation.

Errors in the results were estimated to be of the same order of magnitude as the scatter determined by calibration drops of a measurement series, i.e. ±2.5%.

4. Results

4.1. Addition of tin

Results given in Table 3a and Fig. 1a correspond to the molar enthalpies of mixing of 6-component alloys at 730 K, referred to the pure liquid elements at the same temperature. The reactions can be written as

$$y\mathrm{Bi(liq)} + y\mathrm{Cd(liq)} + y\mathrm{Ga(liq)} + y\mathrm{In(liq)} + y\mathrm{Zn(liq)} + a\mathrm{Sn(liq)}$$

$$\rightarrow \mathrm{Bi}_{y'}\mathrm{Cd}_{y'}\mathrm{Ga}_{y'}\mathrm{In}_{y'}\mathrm{Zn}_{y'}\mathrm{Sn}_{x}\mathrm{(liq)} \quad \text{with} \quad 5y' + x = 1$$

These values, obtained in the mole fraction range $0 < x_{\mathrm{Sn}} < 0.717$, are expressed by

$$\Delta_{\mathrm{mix}} H_m^{\ominus}/\mathrm{J\,mol^{-1}}$$

$$= 3.167 \times 10^3 + 1.477 \times 10^3 x_{\mathrm{Sn}} - 1.787 \times 10^4 x_{\mathrm{Sn}}{}^2 + 2.337 \times 10^4 x_{\mathrm{Sn}}{}^3 - 9.792 \times 10^3 x_{\mathrm{Sn}}{}^4 \qquad (2)$$

Three series of experiments represented by the reaction

$$\mathrm{Bi}_y\mathrm{Cd}_y\mathrm{Ga}_y\mathrm{In}_y\mathrm{Zn}_y\mathrm{(liq,730K} \quad \text{with} \quad y = 0.20) + a\mathrm{Sn}(s\mathrm{,295K})$$

$$\rightarrow \mathrm{Bi}_{y'}\mathrm{Cd}_{y'}\mathrm{Ga}_{y'}\mathrm{In}_{y'}\mathrm{Zn}_{y'}\mathrm{Sn}_{x}\mathrm{(liq)} \quad \text{with} \quad 5y' + x = 1$$

were performed. Here y and y' are the Bi, Cd, Ga, In, Zn mole fractions in the 5-component and 6-component alloys, respectively, and x is the Sn mole fraction in the final 6-component liquid alloy.

4.2. *Addition of bismuth*

Seven series of experiments were performed under the same conditions in the mole fraction range $0 < x_{\mathrm{Bi}} < 0.666$. As before, all the results listed in Table 3b and shown in Fig. 1b are referred to pure elements in the liquid state at the experimental temperature. The enthalpy of formation of the 6-component liquid alloy obtained following the reaction

$$y\mathrm{Cd(liq)} + y\mathrm{Ga(liq)} + y\mathrm{In(liq)} + y\mathrm{Sn(liq)} + y\mathrm{Zn(liq)} + b\mathrm{Bi(liq)}$$

$$\rightarrow \mathrm{Cd}_{y'}\mathrm{Ga}_{y'}\mathrm{In}_{y'}\mathrm{Sn}_{y'}\mathrm{Zn}_{y'}\mathrm{Bi}_{x}\mathrm{(liq)} \quad \text{with} \quad 5y' + x = 1$$

can be represented by

$$\Delta_{\mathrm{mix}} H_m^{\ominus}/\mathrm{J\,mol^{-1}}$$

$$= 3.151 \times 10^3 + 1.165 \times 10^3 x_{\mathrm{Bi}} - 1.508 \times 10^4 x_{\mathrm{Bi}}{}^2 + 1.861 \times 10^4 x_{\mathrm{Bi}}{}^3 - 7.847 \times 10^3 x_{\mathrm{Bi}}{}^4 \qquad (3)$$

To obtain the experimental enthalpies of mixing following the two approaches used, we must know the enthalpy of formation at the barycenter of the quinary sub-system (Table 2) and the value of $[H_i^{\ominus\mathrm{liq}}(T_{\mathrm{exp}}) - H_i^{\ominus s} T_0]$ with $i = \mathrm{Sn, Bi}$.

This quantity is obtained from Hultgren et al.'s compilation [17]

$$[H_{\mathrm{Sn}}^{\ominus\mathrm{liq}}(730\mathrm{K}) - H_{\mathrm{Sn}}^{\ominus s}(295\mathrm{K})] = 19.545 \times 10^3\,\mathrm{J\,mol^{-1}}$$

$$[H_{\mathrm{Bi}}^{\ominus\mathrm{liq}}(730\mathrm{K}) - H_{\mathrm{Bi}}^{\ominus s}(295\mathrm{K})] = 23.483 \times 10^3\,\mathrm{J\,mol^{-1}}$$

At the barycenter of this 6-component system ($x_i = 0.167$), the values of the enthalpy of formation of the liquid alloy obtained by addition of tin and bismuth are 3036 and 3006 J mol^{-1}, respectively. This good agreement confirms the accuracy of these two sets of experiments.

Table 3a
Results obtained by addition of Sn
m (at the barycenter of quinary system)

$$m = \sum_{i=\mathrm{Bi}}^{i=\mathrm{Zn}} m_i$$

$$m_i = m_{\mathrm{Bi}} = m_{\mathrm{Cd}} = m_{\mathrm{Ga}} = m_{\mathrm{In}} = m_{\mathrm{Zn}}$$

Starting sample[a]	$\Delta m \times 10^3$/ mol (Sn)[b]	ΔQ[c]/J	x_{Sn}[d]	$\Delta_{\mathrm{mix}} H_m^{\ominus}$[e]/ J mol^{-1}
Sample 1 $m \times 10^3 = 4.365$			0	3170
	0.334	7.587	0.071	3169
	0.461	9703	0.154	3020
	0.441	9.462	0.221	3157
	0.722	10.722	0.310	2932
	0.753	14.977	0.383	2801
	0.732	16.001	0.441	2686
	0.742	15.470	0.490	2576
	0.945	15.551	0.540	2464
	1.213	19.841	0.592	2336
	1.39	29.301	0.639	2244
	1.375	28.136	0.676	2157
Sample 2 $m \times 10^3 = 2.547$			0	3170
	0.358	7.957	0.123	3110
	0.456	9.129	0.242	2752
	0.626	11.673	0.361	2179
	0.642	12.113	0.450	1784
	0.752	14.779	0.527	1550
	0.859	16.734	0.592	1327
	0.964	18.396	0.646	1088
	1.139	22.283	0.695	941
	0.661	13.254	0.717	909
Sample 3 $m \times 10^3 = 2.625$			0	3170
	0.293	6.564	0.100	3141
	0.232	5.002	0.167	3056
	0.543	10.714	0.289	2636
	0.483	8.828	0.371	2187
	0.522	9.881	0.441	1875
	0.989	19.618	0.538	1600
	0.672	13.282	0.587	1455
	0.822	16.409	0.634	1335
	0.493	8.416	0.658	1091

[a] Starting sample (in mol).

[b] Amount Δm (in mol) of the pure Sn and Bi dropped.

[c] Measured heat effect.

[d] Molar fraction of added element.

[e] Values of the enthalpies of formation of the Bi + Cd + Ga + In + Sn + Zn liquid system referred to pure liquid elements at T_e.

Table 3b
Results obtained by addition of Bi
m (at the barycenter of quinary system)

$$m = \sum_{i=\mathrm{Cd}}^{i=\mathrm{Zn}} m_i$$

$$m_i = m_{\mathrm{Cd}} = m_{\mathrm{Ga}} = m_{\mathrm{In}} = m_{\mathrm{Sn}} = m_{\mathrm{Zn}}$$

Starting sample[a]	$\Delta m \times 10^3$/ mol (Bi)[b]	ΔQ[c]/J	x_{Bi}[d]	$\Delta_{\mathrm{mix}} H_m^{\ominus}$[e]/ J mol^{-1}
Sample 1 $m \times 10^3 = 3.946$	0		0	3150
	0.275	7.417	0.065	31.75
	0.381	9.994	0.143	3140
	0.127	3.143	0.166	3087
Sample 2 $m \times 10^3 = 9.535$	0		0	3150
	0.604	13.709	0.050	3178
	1.023	25.835	0.138	3049
	0.381	9.585	0.167	3004
Sample 3 $m \times 10^3 = 3.283$	0		0	3150
	0.454	11.957	0.121	3116
	0.203	4.977	0.167	3009
Sample 4 $m \times 10^3 = 6.759$	0		0	3150
	0.506	13.626	0.070	3171
	0.590	15.288	0.140	3116
	0.254	5.912	0.167	3011
Sample 5 $m \times 10^3 = 12.421$	0		0	3150
	0.597	15.927	0.046	3152
	0.867	22.875	0.105	3137
	0.574	13.489	0.141	3013
	0.445	11.089	0.167	2965
Sample 6 $m \times 10^3 = 2.501$	0		0	3150
	0.269	7.17	0.097	3148
	0.219	5.339	0.163	2984
	0.337	8.416	0.248	2831
	0.472	11.087	0.342	2481
	0.253	5.188	0.383	2140
	0.361	8.788	0.433	2038
	0.406	9.886	0.481	1940
	0.566	13.786	0.535	1827
	0.552	13.077	0.579	1675
	0.638	14.980	0.620	1511
	0.908	19.908	0.666	1140
Sample 7 $m \times 10^3 = 3.529$	0		0	3150
	0.238	6.306	0.065	3144
	0.225	5.675	0.119	3064
	0.223	5.352	0.167	2923
	0.187	4.601	0.203	2846
	0.242	5.823	0.245	2724
	0.274	6.778	0.288	2643
	0.282	6.578	0.328	2486
	0.499	12.196	0.388	2351

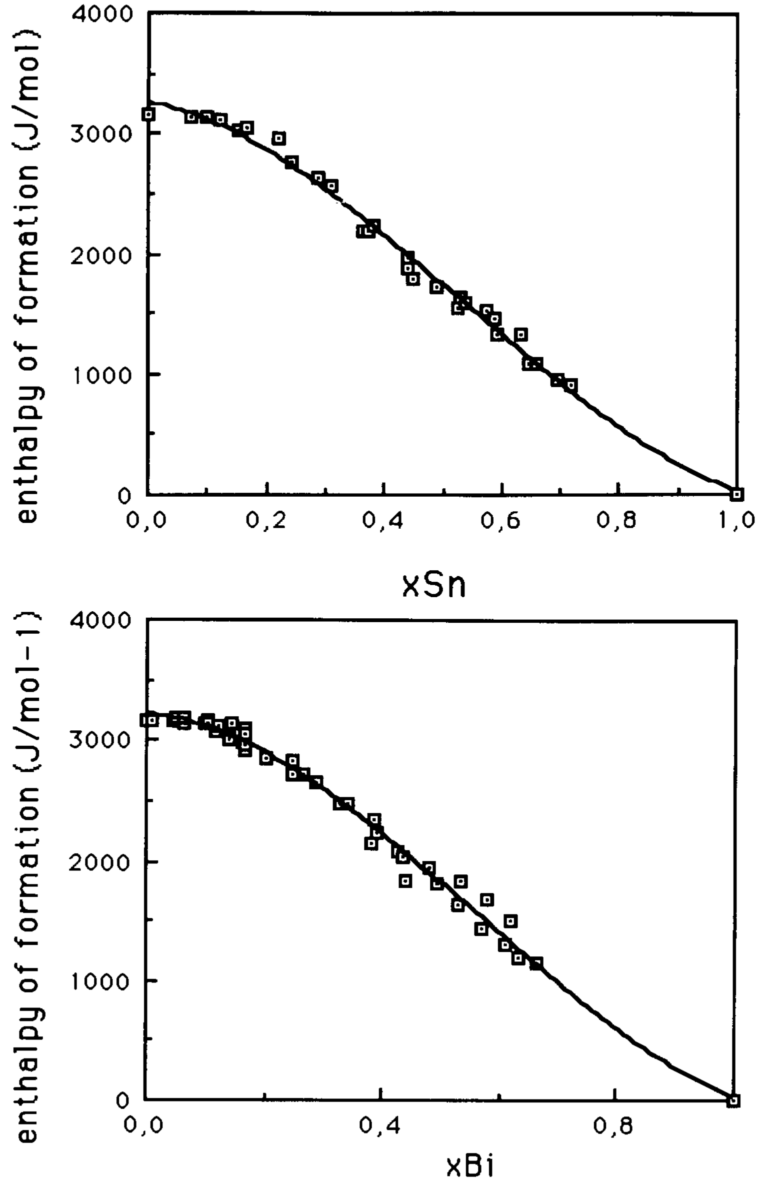

Fig. 1. a. Experimental values (○) of the molar enthalpy of formation of the Bi + Cd + Ga + In + Sn + Zn liquid system obtained by addition of pure tin at 730 K. The curve (——) corresponds to Eq. (2). b. Experimental values (○) of the molar enthalpy of formation of the Bi + Cd + Ga + In + Sn + Zn liquid system obtained by addition of pure bismuth at 730 K. The curve (——) corresponds to Eq. (3).

From these measurements, partial mixing molar enthalpies of tin and bismuth ($H_{\mathrm{Sn}}^{\ominus} = ((\partial \Delta_{\mathrm{mix}} H_m^{\ominus})/\partial x_{\mathrm{Sn}})$, for example) along the two studied sections of this 6-component system can be obtained, respectively. Therefore these values will be obtained with a better agreement if the starting sample is more important; with this condition the necessary amount of tin (or bismuth) Δm_i could be assimilated to ∂m_i. As this study was not performed with this aim, these conditions were not respected and so the values obtained (not listed here) show a large discrepancy.

5. Discussion

In a recent publication, Perona-Silhol et al. [1] described the difficulties in predicting the excess functions of 5-component systems. Several models or relationships are available to describe the molar enthalpy of formation of an *n*-component system but the selection a priori of the best formula is quite difficult. However, this choice becomes easier if some comparative experimental data are known.

In the case of the Bi + Cd + Ga + In + Sn + Zn liquid system, the enthalpy of formation has been calculated using three relationships: two symmetrical relationships proposed by Kohler [18] and Muggianu et al. [19] respectively, and one asymmetrical relationship given by Toop [20]. All these calculations were performed with the assumption that the enthalpies of formation of the limiting binary alloys are not temperature-dependent. Kohler's equation [18] is

$$\Delta_{\mathrm{mix}} H_m^{\ominus} = \textstyle\sum_{ij}(x_i + x_j)^2 \Delta_{\mathrm{mix}} H_{m(i,j)}^{\ominus}$$

Muggianu's equation [19] is

$$\Delta_{\mathrm{mix}} H_m^{\ominus} = \textstyle\sum_{ij}\{(4x_i x_j)/(1 + x_i - x_j)(1 + x_j - x_i)\} \Delta_{\mathrm{mix}} H_{m(i,j)}^{\ominus}$$

Toop's equation [20] is

$$\Delta_{\mathrm{mix}} H_m^{\ominus} = \textstyle\sum_{ij}(x_j + x_k)^2 \Delta_{\mathrm{mix}} H_{m(j,k)}^{\ominus} + \textstyle\sum_{ij}\{x_j/(1 - x_i)\} \Delta_{\mathrm{mix}} H_{m(j,k)}^{\ominus}$$

Only the enthalpies of formation of the limiting binary systems are needed and a complete description of the use of these relations has been published [15]. All calculated values of the $\Delta_{\mathrm{mix}} H_m^{\ominus}$ functions are listed in Table 4. The calculations with the asymmetrical relation [20] are based on the pure components: Bi, Cd, Ga, In, Sn and Zn.

We have also calculated the enthalpy of formation using a model proposed by Hoch and Arpshofen [21, 22]. This model assumes the existence of complexes of *n* atoms in solution and, in this case, only binary interactions ($w_{i,j}$) are taken into account.

The Hoch–Arpshofen equation [21] is

$$\Delta_{\mathrm{mix}} H_m^{\ominus} = \textstyle\sum_{jk} w_{ij}\, n_{ij} \{1 - (1 - x_j)^{(n_{ij} - 1)}\}$$

The results are listed in Table 4. This table provides a comparison between the experimental and predicted values obtained using the symmetrical relations (Kohler and Muggianu). In this case the discrepancy (of about 10%) is larger than the experimental uncertainty. However, using Toop's relation based on Bi or Sn, the differences between experimental and calculated values are less than 5%. This may be connected with the existence of definite compounds in the limiting binary systems (Bi + In and In + Sn).

Results obtained with Hoch's relationship (using only one interaction parameter ($w_{i,j}$) to describe all the enthalpies of formation of liquid binary alloys) are outside the

Table 4
Integral molar enthalpy of formation of the Bi + Cd + Ga + In + Sn + Zn liquid system: experimental (column 2) and predicted values (in J mol^{-1}) using the relations proposed by Kohler (column 3), Muggianu (column 4), Toop (columns 5–10) with the asymmetry based on Bi, Cd, Ga, In, Sn and Zn, respectively, and Hoch (column 11).

With $\sigma^\ominus = \left[\sum_{r=0}^{r=n} (H^\ominus_{\mathrm{exp}} - H^\ominus_{\mathrm{calc}})^2/(n-1) \right]^{1/2}$

x_{Bi}	$\Delta_{\mathrm{mix}} H^\ominus_m$ exp	$\Delta_{\mathrm{mix}} H^\ominus_m$ [18]	$\Delta_{\mathrm{mix}} H^\ominus_m$ [19]	$\Delta_{\mathrm{mix}} H^\ominus_m$ [20] /Bi	$\Delta_{\mathrm{mix}} H^\ominus_m$ [20] /Cd	$\Delta_{\mathrm{mix}} H^\ominus_m$ [20] /Ga	$\Delta_{\mathrm{mix}} H^\ominus_m$ [20] /In	$\Delta_{\mathrm{mix}} H^\ominus_m$ [20] /Sn	$\Delta_{\mathrm{mix}} H^\ominus_m$ [20] /Zn	$\Delta_{\mathrm{mix}} H^\ominus$ [20]
0.0	3151	2857	2857	2857	2862	2932	2976	3187	2696	3354
0.1	3134	2764	2692	2981	2770	2798	2907	3059	2542	3336
0.2	2916	2573	2479	2825	2559	2525	2669	2736	2342	3176
0.3	2579	2374	2239	2542	2302	2229	2383	2448	2126	2901
0.4	2188	2158	1977	2213	1995	1914	2050	2149	1863	2538
0.5	1787	1910	1685	1869	1651	1583	1686	1824	1558	2114
0.6	1403	1624	1362	1513	1290	1243	1310	1476	1229	1654
0.7	1043	1292	1012	1133	929	904	940	1111	894	1187
0.8	695	913	648	729	585	576	590	739	569	737
0.9	331	482	296	326	272	270	273	367	268	333
σ		295	354	141	304	321	210	131	482	260

range of the experimental uncertainty. To improve the predictions with this model, a better analytical description of the enthalpy of formation of the binary systems that exhibit an immiscibility gap (Bi + Ga, Bi + Zn and Cd + Ga) seems necessary.

6. Conclusion

At 730 K, from the enthalpies of formation of the Cd + Ga + In + Sn + Zn and Bi + Cd + Ga + In + Zn liquid systems previously determined, the enthalpy of formation of the Bi + Cd + Ga + In + Sn + Zn liquid system has been measured by direct high-temperature calorimetry. Using the corresponding data of the 15 limiting binary systems, the enthalpy of formation of the Bi + Cd + Ga + In + Sn + Zn system has been calculated. Taking into account the experimental uncertainty, Toop's asymmetrical relation provides the best predicted values.

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