Journal of Alloys and Compounds, 189 (1992) 17–22
JALCOM 358

The Cd–Ga–In–Sn–Zn liquid system. Experimental and predicted values of the enthalpy of formation

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(Received February 19, 1992)

Abstract

Using a high-temperature Calvet calorimeter, the enthalpy of formation of the Cd–Ga–In–Sn–Zn liquid alloy was determined at 730 K. For the investigated molar fraction range, the enthalpy of formation of this alloy is positive. The experimental results were compared with the values predicted using the thermodynamic data of the limiting binary systems and the Hoch–Arpshofen model extended to the multicomponent alloys: $\Delta_{\mathrm{mix}}H_{\mathrm{m}} = \Sigma_{ij} W_{ij} n_{ij} x_i \{1-(1-x_j)^{n_{ij}-1}\}$. The parameters W_{ij} and the integers n_{ij} were deduced from published binary enthalpy data. Taking all the uncertainties into account, the agreement between the calculated and experimental data is satisfactory. Therefore the Hoch–Arpshofen model allows a correct prediction of the excess molar function of formation of the Cd–Ga–In–Sn–Zn liquid alloy.

1. Introduction

New alloys for specific uses are generally composed of a large number of metals. Consequently, determinations of their physicochemical properties are expensive and time consuming. Therefore the development of theoretical and empirical formulae which predict the thermodynamic properties of *n*-component alloys is of interest.

The aim of this paper is to compare the experimental values of the enthalpy of formation of the Cd–Ga–In–Sn–Zn liquid alloy with the corresponding values obtained using the data of the limiting binary systems and the Hoch–Arpshofen (HA) relation.

2. Literature data

Theoretically, the enthalpies of formation of subsystems (binary, ternary, quaternary) are not required for the determination, by calorimetry, of the enthalpy of formation of an *n*-component alloy. However, a knowledge of the enthalpy of mixing of the subsystems is essential for application of the HA relation (with binary systems) and to check the experimental results. Therefore, in the next section, we describe the enthalpies of formation of the limiting binary alloys and the main characteristics of their equilibrium phase diagrams; the latter information enables the correct temperature and molar fraction ranges to be chosen to perform the calorimetric determinations with liquid alloys.

2.1. Binary alloys

2.1.1. Cd–Ga system

In the phase diagram the liquidus curve exhibits a eutectic point very close to gallium ($T_{\mathrm{E}}=302.53$ K; $x_{\mathrm{Cd}}=0.003$) and a flat miscibility gap. The coordinates of the monotectic and critical points are $T_{\mathrm{M}}=555$ K with $x_{\mathrm{Cd}}=0.773$ and $T_{\mathrm{C}}=568$ K with $x_{\mathrm{Cd}}=0.5$ respectively [1].

In the liquid state, the enthalpies of mixing obtained by Vecher and Mechkovskii [2] at 630 K are in agreement with the values of Kleppa [3] compiled by Hultgren *et al.* [4] (Table 1, see later). At $x_{\mathrm{Cd}}=0.5$, Vecher and Mechkovskii [2] and Kleppa [3] proposed values of 2620 J mol^{-1} and 2665 J mol^{-1} respectively; both results were obtained by direct calorimetry. The values of Vecher and Mechkovskii were used to calculate the mixing enthalpy of formation from our experimental data. The recent values obtained by Moser *et al.* [5] at 602 and 698 K present a temperature dependence with a mean value of ΔC_p of about 5.7 J K^{-1} mol^{-1} in this temperature range.

0925-8388/92/$5.00

In order for the calculation to be meticulously homogeneous and coherent, Hultgren's values were used when they were available.

2.1.2. Cd–In system

Two intermediate phases (β phase (399 K<T<469 K with 0.17<x_{In}<0.255) and γ phase (399 K with 0.808 <x_{In}<0.95)) have been found and the eutectic point is in the indium-rich zone (T_{E}=401 K and x_{In}=0.743). The solid solubility of cadmium in indium is large (x_{Cd}=0.18 at 393 K) [6].

The enthalpy data of Wittig and Müller [7] and Kleppa [3] at 723 K are in good agreement; therefore the values selected by Hultgren *et al.* [4] have been retained for this study (Table 1, see later).

2.1.3. Cd–Sn system

The phase diagram [8] exhibits a eutectic point (x_{Sn}=0.6655 at T_{E}=449 K) and an intermediate solid phase (β) of simple hexagonal A3 structure. The coordinates of the peritectic and eutectoid points are T=496 K with x_{Sn}=0.99 and T=406 K with x_{Sn}=0.947. The limiting solid solubilities are x_{Sn}=0.0024 at T=449 K and x_{Cd}=0.0063 at 496 K.

As for the Cd–In system we have used the enthalpies of mixing obtained by Kleppa [9] at 623 and 723 K and selected by Hultgren *et al.* [4] (Table 1, see later).

2.1.4. Cd–Zn system

The liquidus curve of the phase diagram [10] exhibits only a eutectic point located near pure cadmium (T_{E}=539 K; x_{Zn}=0.2656). The limiting solid solubilities at T_{E} are x_{Zn}=0.05 and x_{Cd}=0.013.

The enthalpies of mixing reported by Hultgren *et al.* [4] (Table 1, see later) (selected from the calorimetric experiments of Kleppa [11] and Wittig *et al.* [12]) were used.

2.1.5. Ga–In system

From ref. 13, the eutectic point of the phase diagram is located at x_{In}=0.142 with T_{E}=288.5 K; at this temperature the limiting solid solubility of gallium in indium is x_{Ga}=0.022.

The enthalpies of mixing obtained by calorimetry by Bros [14] at 743 K and by Predel and Stein [15] at 623 K and selected by Hayes and Kubaschewski [16] are in good agreement. The experimental values of Bros [14] are given in Table 1.

2.1.6. Ga–Sn system

The phase diagram is very simple [6]; the liquidus curve exhibits a eutectic point situated near pure gallium (T_{E}=293.7 K at x_{Ga}=0.915) and, at this temperature, the solid solubilities are x_{Ga}=0.071 and x_{Sn}=1.7×10^{-4}.

We have selected (Table 1) the calorimetric results on the enthalpy of mixing obtained by Bros and Laffitte [17] at 743 K.

2.1.7. Ga–Zn system

The phase diagram [18] shows a eutectic point displaced near gallium (T_{E}=297.82 K; x_{Zn}=0.0387). The maximum solid solubilities are x_{Zn}=0.008 at 293 K and x_{Ga}=0.03 at about 533 K.

The enthalpies of mixing (Table 1) compiled by Hultgren *et al.* [4] are in agreement with those obtained by Gambino [19].

2.1.8. In–Sn system

The phase diagram exhibits a central eutectic point (x_{Sn}=0.483, T_{E}=393 K) and a complex solid region with two intermediate phases β and γ [6].

Wittig and Scheidt [20], Kleppa [21] and Bros and Laffitte [22] have determined the enthalpy of formation by calorimetry. In Table 1 the values selected by Hultgren *et al.* [4] are reported.

2.1.9. In–Zn system

In the phase diagram [23] the liquidus curve exhibits a eutectic point situated near pure indium (T_{E}=416.7 K; x_{In}=0.962) and the limits of the solid solubility of indium in zinc and of zinc in indium are about 0.12 at.% In and 2.06 at.% Zn at the eutectic temperature.

The experimental values of the enthalpy of mixing obtained by Wittig and Müller [7] at 733 K and by Kleppa [11] at 723 K, and selected by Hultgren *et al.* [4], have been retained for this study (Table 1).

2.1.10. Sn–Zn system

From the phase diagram of Moser *et al.* [24], the eutectic point is located at x_{Sn}=0.85, T_{E}=471.7 K. The limiting solid solubilities are x_{Zn}=6×10^{-3} and x_{Sn}=4×10^{-4} at the eutectic temperature.

The enthalpies of mixing obtained by Kleppa [11] at 703 and 798 K (Table 1) and selected by Hultgren *et al.* [4] were used.

At the experimental temperature of 730 K, all binary alloys are liquid and, from the shape of the binary phase diagrams, we can predict that the ternary, quaternary and five-component alloys will also be liquid.

2.2. Ternary alloys

The integral thermochemical values of the ten limiting ternary systems are not available. The enthalpies of formation of the six equimolar liquid ternary alloys used are reported in Table 2.

2.3. Quaternary alloys

The enthalpies of formation of the following quaternary systems were determined by direct calorimetry

TABLE 1. Enthalpies of formation (*vs.* molar fraction) of the limiting liquid binary systems ($\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ in J mol^{-1})

x_{Ga}[a]	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$	x_{In}[b]	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$	x_{Sn}[c]	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$	x_{Zn}[d]	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$	x_{In}[e]	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$
0.1	1221	0.1	628	0.1	820	0.1	774	0.1	410
0.2	1966	0.2	1046	0.2	1360	0.2	1372	0.2	720
0.3	2389	0.3	1301	0.3	1674	0.3	1761	0.3	935
0.4	2611	0.4	1427	0.4	1807	0.4	2008	0.4	1065
0.5	2665	0.5	1431	0.5	1803	0.5	2092	0.5	1115
0.6	2577	0.6	1326	0.6	1674	0.6	2025	0.6	1090
0.7	2305	0.7	1117	0.7	1431	0.7	1799	0.7	970
0.8	1828	0.8	820	0.8	1075	0.8	1397	0.8	765
0.9	1038	0.9	444	0.9	598	0.9	803	0.9	445

x_{Sn}[f]	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$	x_{Zn}[g]	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$	x_{Sn}[h]	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$	x_{Zn}[i]	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$	x_{In}[j]	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$
0.1	335	0.1	494	0.1	−84	0.1	1021	0.1	845
0.2	585	0.2	895	0.2	−138	0.2	1874	0.2	1623
0.3	755	0.3	1205	0.3	−176	0.3	2540	0.3	2289
0.4	845	0.4	1431	0.4	−197	0.4	2996	0.4	2791
0.5	865	0.5	1569	0.5	−197	0.5	3230	0.5	3096
0.6	820	0.6	1598	0.6	−184	0.6	3226	0.6	3188
0.7	705	0.7	1502	0.7	−159	0.7	2962	0.7	3054
0.8	535	0.8	1234	0.8	−121	0.8	2393	0.8	2615
0.9	300	0.9	757	0.9	−71	0.9	1452	0.9	1711

[a] Cd–Ga system, ref. 4. [b] Cd–In system, ref. 4. [c] Cd–Sn system, ref. 4. [d] Cd–Zn system, ref. 4. [e] Ga–In system, ref. 14. [f] Ga–Sn system, ref. 17. [g] Ga–Zn system, ref. 4. [h] In–Sn system, ref. 4. [i] In–Zn system, ref. 4. [j] Sn–Zn system, ref. 4.

TABLE 2. Experimental and calculated (with HA model) data of the enthalpy of formation of liquid binary, ternary and quaternary alloys at the equimolar composition ($\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ in J mol^{-1})

System	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ (exp.)	T (K)	Reference	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ (calc.)	T (K)	Reference
Cd–Ga[a]	2620	630	2	2665	700	4
Cd–In	1431	723	4	1431		
Cd–Sn	1803	723	4	1803		
Cd–Zn	2092	800	4	2092		
Ga–In	1115	623	14	1115		
Ga–Sn	865	743	17	865		
Ga–Zn	1799	723	19	1569	723	4
In–Sn	−185	750	22	−197	700	4
In–Zn	3230	700	4	3230		
Sn–Zn	3096	750	4	3096		
Cd–Ga–In[b]	2240	630	2	2515		
Cd–Ga–Sn	2580	730	28	2582		
Cd–Ga–Zn	2850	730	28	3141		
Ga–In–Sn	797	521	25	812		
Ga–In–Zn	2803	723	26	3053		
Ga–Sn–Zn	2531	723	27	2949		
Cd–Ga–In–Sn[c]	2036	730		2157		
Cd–Ga–In–Zn	3096	730		3428		
Ga–In–Sn–Zn	2325	730		2903		

[a] Molar fraction of each component, 0.5. [b] Molar fraction of each component, 0.33. [c] Molar fraction of each component, 0.25.

at 730 K by Perona-Silhol [28]. Only the data corresponding to the composition of the barycenter are given here (see also Table 2).

2.3.1. Ga–In–Sn–Zn system

The mean value of $\Delta_{\mathrm{mix}}H_{\mathrm{m}} = 2325$ J mol^{-1} was obtained by dropping: (a) zinc in the equimolar Ga–In–Sn liquid alloy ($\Delta_{\text{mix}}H_{\text{m}}=2269$ J mol^{-1}); (b) tin in the equimolar Ga–In–Zn liquid alloy ($\Delta_{\text{mix}}H_{\text{m}}=2364$ J mol^{-1}); (c) indium in the equimolar Ga–Sn–Zn liquid alloy ($\Delta_{\text{mix}}H_{\text{m}}=2343$ J mol^{-1}).

2.3.2. Cd–Ga–In–Sn system

The mean value of $\Delta_{\text{mix}}H_{\text{m}}=2036$ J mol^{-1} was obtained by dropping: (a) cadmium in the equimolar Ga–In–Sn liquid alloy ($\Delta_{\text{mix}}H_{\text{m}}=1666$ J mol^{-1} (not used in calculation of mean)); (b) tin in the equimolar Cd–Ga–In liquid alloy ($\Delta_{\text{mix}}H_{\text{m}}=1985$ J mol^{-1}); (c) indium in the equimolar Cd–Ga–Sn liquid alloy ($\Delta_{\text{mix}}H_{\text{m}}=2087$ J mol^{-1}).

2.3.3. Cd–Ga–In–Zn system

The mean value of $\Delta_{\text{mix}}H_{\text{m}}=3096$ J mol^{-1} was obtained by dropping: (a) cadmium in the equimolar Ga–In–Zn liquid alloy ($\Delta_{\text{mix}}H_{\text{m}}=2998$ J mol^{-1}); (b) indium in the equimolar Cd–Ga–Zn liquid alloy ($\Delta_{\text{mix}}H_{\text{m}}=3195$ J mol^{-1}); (c) zinc in the equimolar Cd–Ga–In liquid alloy ($\Delta_{\text{mix}}H_{\text{m}}=2559$ J mol^{-1} (not used in calculation of mean)).

3. Experimental details

3.1. Materials

Cadmium (99.999 at.% Cd) and zinc (99.999 at.% Zn) were supplied by Prolabo. Gallium (99.995 at.% Ga), indium (99.999 at.% In) and tin (99.999 at.% Sn) were obtained from Koch-Light Co. High-purity metals (cadmium, indium, tin, zinc) were rinsed with pure acetone, dried and cut into small pieces. The gallium was melted in a warm dilute solution of hydrochloric acid in water, divided into small droplets and dried after washing with cold distilled water.

During calorimetric experiments pure liquid metals were protected by a purified argon atmosphere (Argon U from Air Liquide Co.).

The alloying process was performed in thin-walled crucibles of pure graphite (inside diameter, 6 mm; height, 40 mm) located in a gas-tight silica cell. A complete description of the experimental cell has been published previously [28].

3.2. Method

Quaternary and five-component enthalpies of mixing were measured at 730 K using a Calvet high-temperature calorimeter [29] by the direct drop method [19]. Alloys were formed by multiple successive additions of the fourth (or the fifth) metal in the ternary (or quaternary) liquid alloy. The calorimeter was equipped with an automated sample charger which distributed automatically the added samples of metal.

The calorimeter was calibrated either from the first additions of the pure element or from additions of α-alumina crystals (National Institute of Standards and Technology (NIST), US Department of Commerce, Washington DC 20234, USA). To calibrate the calorimeter and to refer the final results to the liquid state, the enthalpy contents of the added metals were taken from Hultgren *et al.* [4].

Using a calculation described by Hatem [30], the errors of the enthalpies of formation of the five-component alloys were estimated to be about ±9%. The temperature uncertainty was about ±1 K.

4. Results

The enthalpies of formation of six liquid ternary alloys and three liquid quaternary alloys are given in Table 2. The experimental and predicted (using the HA model) data are given in columns 2 and 5 respectively. The discrepancies between the measured and calculated data are less for the ternary alloys than for the quaternary systems.

To obtain the enthalpy of formation of the five-component liquid alloy at $x_{\text{Ga}}=x_{\text{Cd}}=x_{\text{In}}=x_{\text{Sn}}=x_{\text{Zn}}=0.20$ (barycenter), cadmium samples (or tin or zinc) were dropped in equimolar liquid Ga–In–Sn–Zn (or Cd–Ga–In–Zn or Gd–Ga–In–Sn) at 730 K. The results are collected in Table 3 and reported in Figs. 1–3.

5. Discussion

The HA model [31, 32] was deduced from physical principles and is applicable to multicomponent systems [28]. Let us briefly recall this model. It relies on the existence of "complexes" in solution and on the strength of the bond between the different atoms. One feature of this model is that it only considers binary interaction. It is for this reason that only binary data are needed for all systems.

For a binary system (*ij*), the molar integral and partial enthalpies can be represented by

$$\Delta_{\text{mix}}H_{\text{m}}=W_{ij}n_{ij}(x_i-x_i^{n_{ij}})$$

$$\Delta H_i=W_{ij}n_{ij}\{1-n_{ij}x_i^{(n_{ij}-1)}+(n_{ij}-1)x_i^{n_{ij}}\}$$

$$\Delta H_j=W_{ij}n_{ij}(n_{ij}-1)x_i^{n_{ij}}$$

For a multicomponent solution (*i*, *j*, *k*, *l*, . . .) with the mole fractions (x_i, x_j, x_k, x_l, . . .), the molar enthalpy of mixing is

$$\Delta_{\text{mix}}H_{\text{m}}=\sum_{ij}W_{ij}n_{ij}x_i\{1-(1-x_j)^{n_{ij}-1}\}$$

From the binary data given in Table 1, the interaction terms (W_{ij}) ($W_{ij}=\Delta_{\text{mix}}H_{\text{m}}/n_{ij}$ $(x_i-x^{n_{ij}})$ where x_i is the

TABLE 3. Comparison between experimental and calculated (with HA model) enthalpies of formation of the Cd–Ga–In–Sn–Zn liquid alloys at 730 K. In columns 1, 2 and 3 are listed the mixing enthalpies obtained by addition of tin, zinc and cadmium to the corresponding quaternary equimolar liquid alloys ($\Delta_{mix}H_m$ in J mol^{-1})

x_{Sn}	$\Delta_{mix}H_m$ (exp.)	$\Delta_{mix}H_m$ (calc.)	x_{Zn}	$\Delta_{mix}H_m$ (exp.)	$\Delta_{mix}H_m$ (calc.)	x_{Cd}	$\Delta_{mix}H_m$ (exp.)	$\Delta_{mix}H_m$ (calc.)
0.000	3096	3428	0.000	2036	2157	0.000	2325	2903
0.071	3116	3469	0.067	2582	2638	0.029	2572	2999
0.136	2691	3440	0.103	3171	2864	0.064	2886	3102
0.154	2803	3421	0.115	3452	2934	0.088	2812	3163
0.196	2744	3361	0.200	3586	3354	0.103	3093	3198
0.253	2563	3245	0.226	3423	3456	0.105	2873	3202
0.268	2496	3208	0.269	3301	3595	0.123	3042	3240
0.301	2458	3120	0.292	3598	3655	0.149	2968	3287
0.320	2524	3063	0.372	3799	3783	0.176	3159	3326
0.401	2379	2788	0.375	3841	3785	0.200	3188	3354
0.420	2215	2715	0.399	3770	3797	0.256	3379	3390
0.461	2271	2551	0.407	4130	3799	0.265	3443	3392
0.481	1919	2466	0.435	3971	3793	0.315	3496	3385
0.505	2003	2362	0.460	3925	3775	0.326	3510	3379
0.510	1761	2340	0.461	3820	3774	0.352	3628	3359
0.539	1622	2209	0.498	3904	3721	0.411	3510	3281
0.600		1923	0.507	3925	3704	0.439	3593	3229
0.700		1431	0.521	3715	3674	0.469	3383	3161
0.800		932	0.543	3887	3619	0.526	3283	3001
0.900		447	0.548	3720	3605	0.617	3058	2656
1.000	0	0	0.566	3782	3550	0.700		2247
			0.654	3568	3179	0.800		1632
			0.700		2917	0.900		884
			0.800		2181	1.000	0	0
			0.900		1211			
			1.000	0	0			

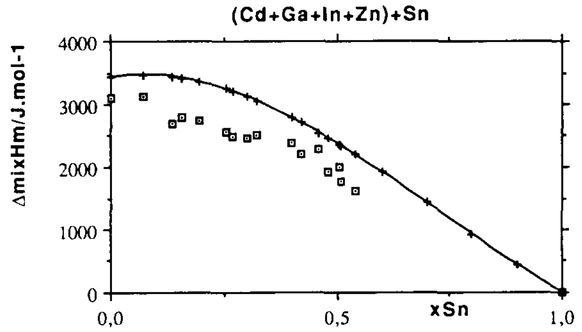

Fig. 1. Enthalpy of formation of the Cd–Ga–In–Sn–Zn liquid alloy obtained by addition of tin to the equimolar Cd–Ga–In–Zn solution at 730 K: ☐, experimental; +, calculated (HA model).

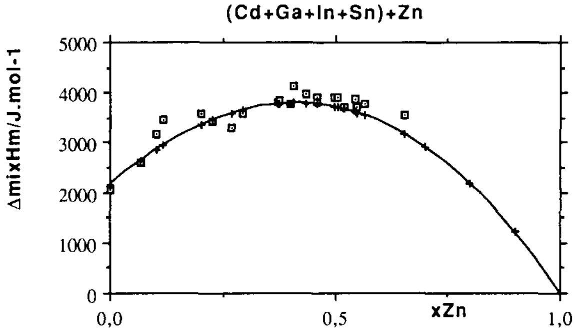

Fig. 2. Enthalpy of formation of the Cd–Ga–In–Sn–Zn liquid alloy obtained by addition of zinc to the equimolar Cd–Ga–In–Sn solution at 730 K; ☐, experimental; +, calculated (HA model).

molar fraction of component i with $x_i > 0.5$ for an extremum of $\Delta_{mix}H_m$) and parameters n_{ij} were deduced. The values of W_{ij}, W_{ij}/R and n_{ij} are reported in Table 4. Table 3 and Figs. 1–3 enable the experimental and calculated results to be compared for the five-component system.

6. Conclusions

The experimental and calculated enthalpies of formation of the five-component liquid alloys (Cd–Ga–In–Sn–Zn) are not in complete agreement over the entire range of concentration. Nevertheless the estimated $\Delta_{mix}H_m$ values for n-component alloys are satisfactory if we consider that (i) the experimental error increases with the number of alloy components and (ii) the calculation of the excess functions using the HA model only requires data on the limiting binary systems. Consequently, where there is a lack of experimental data, the HA model can provide a valuable

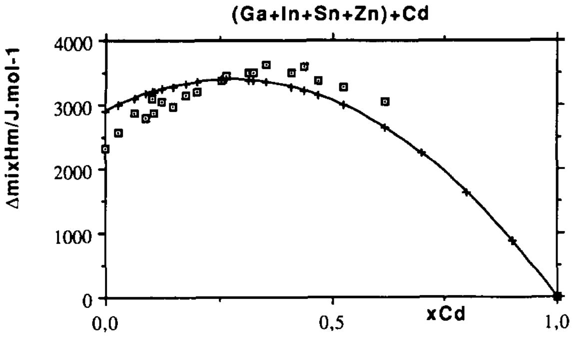

Fig. 3. Enthalpy of formation of the Cd–Ga–In–Sn–Zn liquid alloy obtained by addition of cadmium to the equimolar Ga–In–Sn–Zn solution at 730 K; □, experimental; +, calculated (HA model).

TABLE 4. The values of n_{ij}, W_{ij}/R and W_{ij} (in kK and J) for each binary system

System	Reference	n_{ij}	i	W_{ij}/R (kK)	+/−	W_{ij} (J)
Cd–Ga	4	2	Cd	0.6951	0.0538	5778
Cd–In	4	3	Cd	0.1571	0.0115	1306
Cd–Sn	4	3	Cd	0.2031	0.0180	1688
Cd–Zn	4	2	Cd	0.5143	0.0107	4276
Ga–In	14	2	Ga	0.2737	0.0084	2275
Ga–Sn	17	2	Sn	0.2097	0.0082	1744
Ga–Zn	4	3	Zn	0.1764	0.0103	1466
In–Sn	4	2	Sn	−0.0488	0.0032	−406
In–Zn	4	3	Zn	0.3582	0.0271	2978
Sn–Zn	4	3	Zn	0.3641	0.0203	3027

approach to the determination of thermodynamic excess functions of a multicomponent alloy.

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