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The enthalpy of formation of the Cd–Ga–Zn liquid system

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Abstract

Using a high-temperature Calvet calorimeter, the molar enthalpies of formation ($\Delta_{\mathrm{mix}}H_{\mathrm{m}} = f(x_{\mathrm{Cd}}, x_{\mathrm{Zn}})$) of the liquid Cd + Ga + Zn alloys were measured at 730 K over a large molar fraction range. The direct drop method (successive additions of solid cadmium and solid zinc) was used to synthesize alloys in the cell of the calorimeter. In agreement with thermodynamic data and equilibrium phase diagrams of limiting binary systems which exhibit either a eutectic point or a miscibility gap, the enthalpy of formation of the liquid Cd + Ga + Zn system is slightly endothermic (extremum value 3.0 kJ mol^{-1}).

Experimental values of $\Delta_{\mathrm{mix}}H_{\mathrm{m}} = f(x_{\mathrm{Cd}}, x_{\mathrm{Zn}})$ are compared with those predicted from the Kohler, Muggianu, Hoch–Arpshofen and Mathieu relations.

INTRODUCTION

The present work is part of a general programme on the thermodynamics of multicomponent liquid alloys formed with low melting-point metals (gallium, indium, tin, cadmium, lead, zinc, . . .) [1, 2].

From a thermodynamic view point, these alloys are characterized by a small enthalpy of formation and no intermetallic compound.

BIBLIOGRAPHIC SURVEY

Phase diagrams of the binary systems and their thermodynamic properties were recently collected and evaluated [3–5].

The equilibrium phase diagrams and the enthalpies of formation of the liquid phase of the three limiting binary systems are summarized below. The three limiting equilibrium phase diagrams redrawn from these references are shown in Fig. 1.

The Cd–Ga system

The equilibrium phase diagram shows a flat liquid miscibility gap, the critical point of which is located at $T_{\mathrm{c}} = 568$ K and $x_{\mathrm{Ga}} = 0.506$. The

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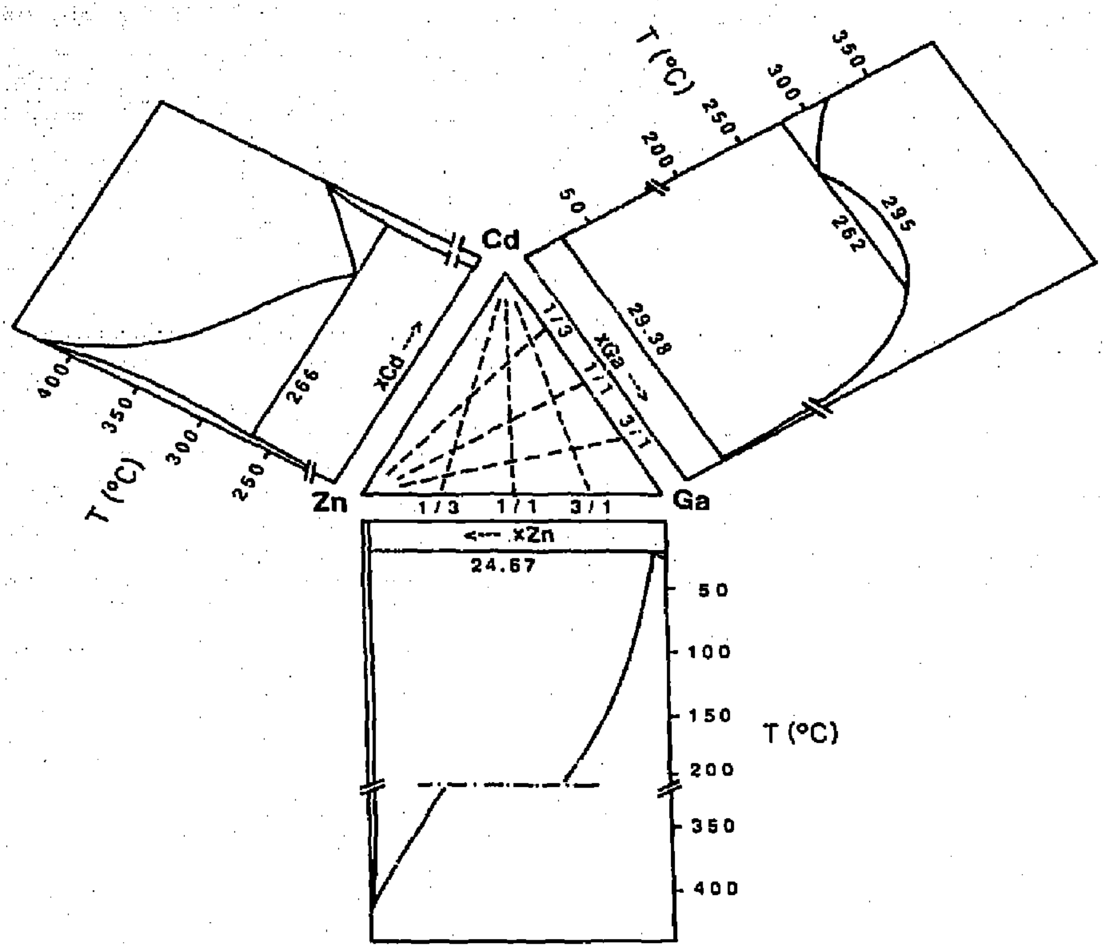

Fig. 1. The binary limiting phase diagrams (Cd + Ga, Cd + Zn and Ga + Zn) redrawn from Refs. 3–5.

coordinates of the monotectic point are $x_{Ga} = 0.227$ with $T_{mon} = 555$ K. In the solid state no extremal solid solution was detected.

In 1988, Moser et al. [3] published a critical compilation of the thermodynamic data related to the formation of this system. The enthalpies of mixing obtained by Vecher et al. [6] (results not included in Moser's compilation) are not far from the earlier values published by Kleppa [7] and reported by Hultgren et al. [8]. Moreover, using these data a correct evaluation of the phase diagram has been obtained. Therefore, the values of Vecher et al. (eqn. (1)) have been used in this study

$$\Delta_{mix}H_m = x_{Cd}(1 - x_{Cd})(13.931 - 15.241x_{Cd} + 16.299x_{Cd}^2 - 0.055x_{Cd}^3) \quad \text{kJ mol}^{-1} \qquad (1)$$

The Cd–Zn system

In 1984, Dutkiewicz and Zakulski [4] published a critical compilation for this binary system. The equilibrium phase diagram exhibits a eutectic point

($x_{Cd} = 0.266$ with $T = 539$ K) and two terminal solid solutions; the maximum solubilities are $x_{Zn} = 0.0435$ at 539 K and $x_{Cd} = 0.0146$ at 593 K.

Several papers on the thermodynamic properties have been published. These data have been given and criticized by Dutkiewicz and Zakulski [4]. The values of the experimental heats of mixing of the liquid Cd + Zn alloy, selected by Hultgren and coworkers [8] may be expressed by the relation

$$\Delta_{mix}H_m = x_{Cd}(1 - x_{Cd})(9.224 - 3.145x_{Cd} + 3.143x_{Cd}^2 - 0.420x_{Cd}^3) \quad \text{kJ mol}^{-1} \qquad (2)$$

The Ga–Zn system

In 1990, Dutkiewicz et al. [5] published a very complete analysis of the thermodynamic data and phase diagram of this system. The equilibrium phase diagram exhibits a eutectic point ($x_{Ga} = 0.036$ and $T_E = 298$ K) near pure gallium. The Zn-rich terminal solid solution has a maximum solubility $x_{Ga} = 0.0236$ at 533 K. At 293 K, the maximum solubility of Zn in gallium is $x_{Zn} = 0.008$. Moreover the available thermodynamic data are consistent within the experimental error and the phase diagram calculated with these thermodynamic data is in good agreement with the experimental one.

From data already published by Gambino [9], the enthalpy of formation of the Ga + Zn liquid system may be expressed by the relation

$$\Delta_{mix}H_m = x_{Zn}(1 - x_{Zn})(5.787 + 2.519x_{Zn} + 0.380x_{Zn}^2 + 0.660x_{Zn}^3) \quad \text{kJ mol}^{-1} \qquad (3)$$

The Cd–Ga–Zn system

In 1976, the equilibrium phase diagram was investigated by differential thermal analysis by Shurai et al. [10]. They found a ternary eutectic mixture with the coordinates, 297.7 K with $x_{Cd} = 0.0535$ and $x_{Ga} = 0.9340$. No particular feature has been noticed for this ternary system.

Because no enthalpy data of the liquid Cd + Ga + Zn system is available, the present investigation was undertaken. From the analysis of the binary and ternary systems, we can expect that, at the experimental temperature (730 K), ternary alloys will be liquid over the entire molar fraction range and, consequently, the enthalpy of mixing was measured by direct calorimetric measurements.

EXPERIMENTAL

Method

The determination of the enthalpies of formation of liquid Cd + Ga + Zn alloys was performed at 730 K using a Calvet high-temperature microcalorimeter described elsewhere [11]. To synthesize alloys in the cell, the direct drop method was applied [9]. In addition, this apparatus was equipped with an automated sample charger [12]: this special thermostated introducer allows twenty samples (15 pieces of pure metal and 5 alumina crystals) to be introduced in the calorimetric cell containing the metallic liquid bath. The main advantages of this automated calorimeter are that the experiments are less time-consuming and, above all, that the reproducibility and, consequently, the precision of the results at high temperature are improved.

The calorimetric crucible was enclosed in a long silica liner (0.65 m), the lower part of which is in good thermal contact with the calorimetric cell. The alloying process takes place in this crucible (about 50 mm in height, 10 mm outer diameter and 9 mm inner diameter), located in the bottom of the cell. The nature of the crucible depends on the reactivity of liquid metals and alloys: during these measurements, pure graphite crucibles were used. Drops were guided from the introducer to the experimental crucible by a thin silica tube. The upper part of this tube, which ends in a funnel, is connected directly to the introducer. With such a device, all the measurements can be performed under vacuum or in a controlled atmosphere.

Following the introduction of the metal, the apparatus was calibrated by adding the alumina crystals.

Generally, before starting a run of measurements, the crucible was charged with about 0.2–0.5 g of the liquid binary alloy.

The experimental temperature was chosen so as to limit the loss of metal during the experiments. Indeed, at 730 K, the vapor pressure of pure cadmium, gallium and zinc are 1.013×10^{2}, 7×10^{-10} and 1.013×10^{1} Pa respectively [13].

Metals, atmosphere and crucibles

High-purity metals (99.999 wt.% tin and cadmium ingot from Koch-Light Company) were used in these experiments. These two metals were rinsed with pure acetone, and dried and cut in small pieces. Gallium (99.999 wt.%) was melted in a dilute solution of hydrochloric acid (5%) in warm water, divided into small droplets and dried after rinsing in cold distilled water.

The crucibles were pure graphite. All experiments were performed in high-purity argon; argon U (from Air Liquid company) was passed over titanium sponge at 1120 K.

Calibration and precision

The calorimeter was calibrated by additions of α-alumina crystals (from NIST [14]) at the end of the experiments.

For two series of measurements performed in the same experimental conditions, in the high temperature range, this completely automated calorimeter provides a reproducibility of less than 2%. Consequently the precision of the enthalpies of formation which depend on several factors (nature of the metals, method of calibration, experimental temperature, ...) is about ±4%.

The error on the molar fraction of the final alloy is less than 1.0%: the difference between the mass of the final alloy and the sum of the metals put into the calorimetric cell was less than 10 mg.

From calibration measurements of the thermocouple (Pt–Pt + 10% Rh) with pure metals, the experimental temperature was determined with an uncertainty of about ±2 K.

RESULTS

Two series of measurements were started with crucibles containing either Cd + Ga liquid alloys or Zn + Ga liquid alloys to which solid zinc (or solid cadmium) were added. The standard deviation of the enthalpies was found to be about 20 or 40 J mol^{-1} for two independent runs at the same molar fraction. To refer all our results to the liquid state, the enthalpy content of the added metals was taken from Hultgren et al. [13].

Table 1 gives the enthalpies of formation (smoothed values) obtained (i) by additions of solid zinc to Cd + Ga liquid alloys with $x_{Cd}/x_{Ga} = 1/3$, 1/1 and 3/1 (Fig. 2a) and (ii) by additions of solid cadmium to Ga + Zn liquid alloys with $x_{Ga}/x_{Zn} = 1/3$, 1/1 and 3/1 (Fig. 2b).

To check the consistency of these results, the enthalpies of formation of alloys of the same composition obtained in these two series have been compared (Table 2). At the same ternary composition, the difference between experimental results obtained either by additions of cadmium or of zinc are generally in good agreement (from 1% to 6%), except at points A and B; for these compositions the values of the enthalpy was deduced by extrapolation.

The isoenthalpic lines have been drawn from the calorimetric results (Fig. 3). In addition, our experimental values of the enthalpy of mixing have been compared with those predicted using the well-known "models for extrapolation" outlined below.

Kohler's relation [16]

$$\Delta_{\mathrm{mix}}H_{\mathrm{m}} = \sum_{\mathrm{ij}} (x_{\mathrm{i}} + x_{\mathrm{j}})^2 [\Delta_{\mathrm{mix}}H_{\mathrm{m(ij)}}]_{x_{\mathrm{i}}/x_{\mathrm{j}}}$$

Muggianu's relation [17]

$$\Delta_{\mathrm{mix}}H_{\mathrm{m}} = \sum_{\mathrm{ij}} [4(x_{\mathrm{i}}x_{\mathrm{j}})/(1 + x_{\mathrm{i}} - x_{\mathrm{j}})(1 + x_{\mathrm{j}} - x_{\mathrm{i}})][\Delta_{\mathrm{mix}}H_{\mathrm{m(ij)}}]_{x_{\mathrm{i(ij)}}=(1-x_{\mathrm{i}}-x_{\mathrm{j}})/2}$$

TABLE 1

Measured (smoothed values) and calculated enthalpies of formation of Cd + Ga + Zn liquid alloys at 730 K with $x_{Cd}/x_{Ga} = 1/3$, 1/1 and 3/1 and with $x_{Ga}/x_{Zn} = 1/3$, 1/1 and 3/1

x_{Cd}	Exp.	Ref. 15	Ref. 16	Ref. 17	Ref. 18	x_{Zn}	Exp.	Ref. 15	Ref. 16	Ref. 17	Ref. 18
$x_{Ga}/x_{Zn} = 1/3$						$x_{Cd}/x_{Ga} = 1/3$					
0.00	1.532	1.615	1.532	1.532	1.586	0.00	2.058	2.086	2.055	2.055	2.616
0.10	2.076	2.155	2.078	2.047	2.178	0.10	2.323	2.323	2.267	2.256	2.742
0.20	2.461	2.535	2.438	2.404	2.588	0.20	2.425	2.504	2.425	2.406	2.824
0.30	2.688	2.757	2.659	2.617	2.822	0.30	2.421	2.615	2.521	2.492	2.847
0.40	2.758	2.822	2.731	2.690	2.884	0.40	2.347	2.638	2.538	2.501	2.795
0.50	2.674	2.732	2.649	2.621	2.782	0.50	2.221	2.556	2.460	2.418	2.651
0.60	2.437	2.488	2.416	2.407	2.521	0.60	2.039	2.353	2.269	2.228	2.399
0.70	2.050	2.091	2.035	2.040	2.106	0.70	1.779	2.013	1.946	1.913	2.024
0.80	1.513	1.543	1.506	1.516	1.544	0.80	1.398	1.518	1.473	1.452	1.510
0.90	0.829	0.846	0.829	0.834	0.840	0.90	0.833	0.853	0.831	0.824	0.841
$x_{Ga}/x_{Zn} = 1/1$						$x_{Cd}/x_{Ga} = 1/1$					
0.00	1.808	1.846	1.806	1.806	1.892	0.00	2.640	2.782	2.637	2.637	3.145
0.10	2.339	2.431	2.380	2.321	2.551	0.10	2.728	2.982	2.802	2.815	3.262
0.20	2.684	2.835	2.679	2.666	2.985	0.20	2.817	3.095	2.895	2.910	3.307
0.30	2.879	3.061	2.867	2.868	3.210	0.30	2.846	3.114	2.917	2.922	3.271
0.40	2.948	3.115	2.945	2.937	3.236	0.40	2.774	3.032	2.857	2.846	3.145
0.50	2.896	2.998	2.879	2.863	3.079	0.50	2.576	2.841	2.702	2.676	2.921
0.60	2.715	2.716	2.642	2.630	2.752	0.60	2.244	2.535	2.438	2.404	2.588
0.70	2.383	2.271	2.223	2.224	2.266	0.70	1.785	2.105	2.049	2.017	2.139
0.80	1.858	1.668	1.629	1.639	1.637	0.80	1.226	1.544	1.522	1.500	1.564
0.90	1.087	0.910	0.879	0.885	0.877	0.90	0.608	0.845	0.843	0.835	0.854
$x_{Ga}x_{Zn} = 3/1$						$x_{Cd}/x_{Ga} = 3/1$					
0.00	1.209	1.154	1.210	1.210	1.252	0.00	2.087	2.086	2.091	2.091	2.101
0.10	2.016	1.934	2.009	1.942	2.187	0.10	2.423	2.464	2.422	2.421	2.488
0.20	2.518	2.504	2.425	2.406	2.824	0.20	2.642	2.716	2.642	2.630	2.752
0.30	2.797	2.869	2.681	2.696	3.188	0.30	2.738	2.841	2.750	2.725	2.888
0.40	2.911	3.031	2.830	2.848	3.301	0.40	2.706	2.837	2.745	2.709	2.895
0.50	2.891	2.996	2.849	2.855	3.186	0.50	2.546	2.702	2.625	2.583	2.767
0.60	2.740	2.767	2.691	2.690	2.867	0.60	2.259	2.434	2.385	2.343	2.502
0.70	2.438	2.349	2.319	2.320	2.365	0.70	1.851	2.032	2.014	1.980	2.096
0.80	1.935	1.746	1.722	1.728	1.705	0.80	1.331	1.494	1.502	1.481	1.546
0.90	1.155	0.961	0.926	0.931	0.909	0.90	0.709	0.817	0.836	0.829	0.849

The Hoch–Arpshofen model [15]

The Hoch–Arpshofen model was deduced from physical principles and is applicable to multi-component systems. For a binary system (ij), the molar integral enthalpies can be represented by means of the equation

$$\Delta_{mix}H_m = W_{ij}n_{ij}(x_i - x_i^{n_{ij}})$$

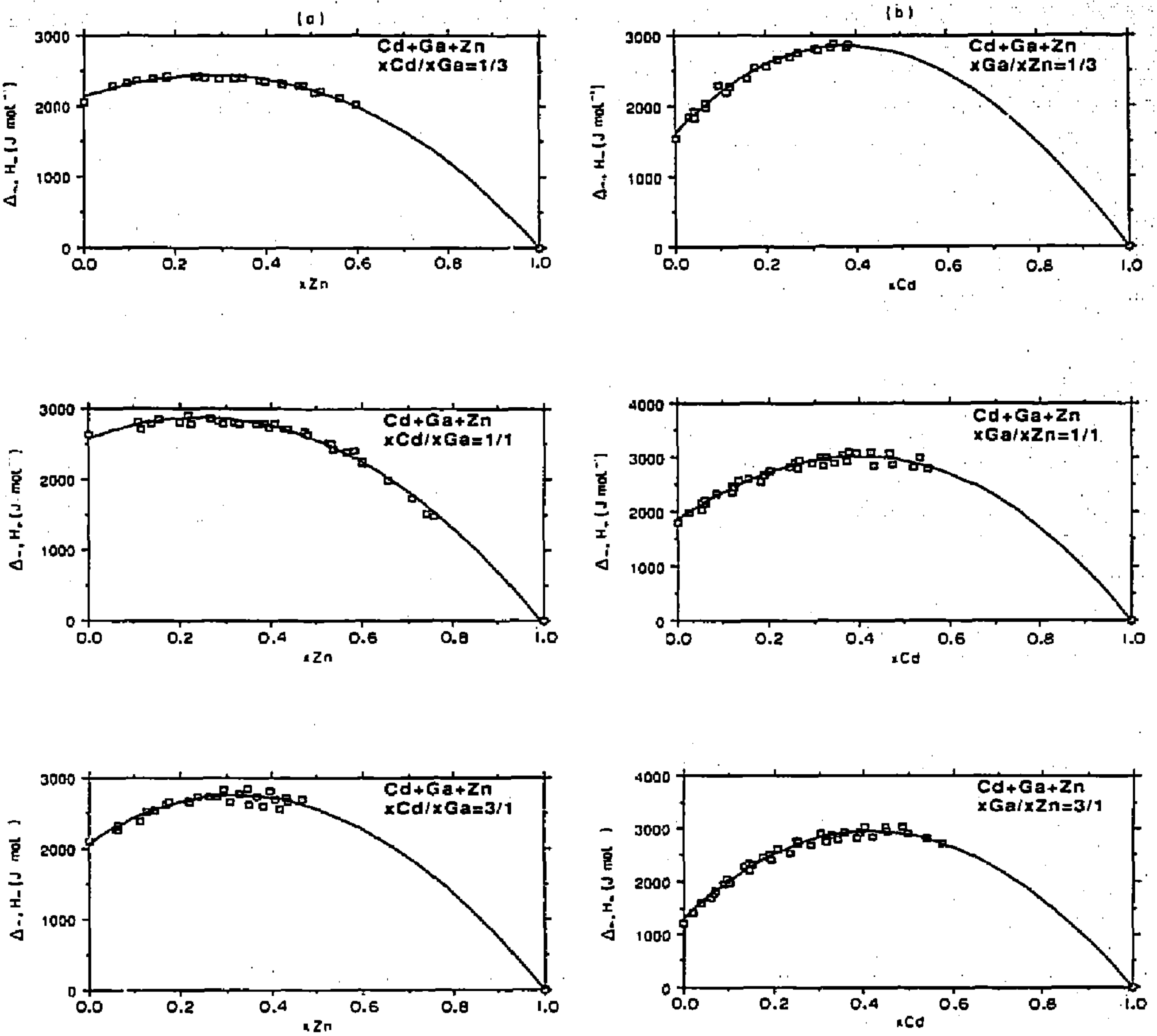

Fig. 2. (a) $\Delta_{mix}H_m = f(x_{Zn})$ along the binary sections $x_{Cd}/x_{Ga} = 1/3$, 1/1 and 3/1; (b) $\Delta_{mix}H_m = f(x_{Cd})$ along the binary sections $x_{Ga}/x_{Zn} = 1/3$, 1/1 and 3/1.

For a multi-component solution (i, j, k, l, ...) with the molar fractions $(x_i, x_j, x_k, x_l, \ldots)$, the molar enthalpy of mixing is

$$\Delta_{mix}H_m = \sum_{ij} W_{ij} n_{ij} x_i [1 - (1 - x_j)^{n_{ij}-1}]$$

The interaction terms (W_{ij}) $(W_{ij} = \Delta_{mix}H_{m(ij)}/[n_{ij}(x_i - x_i^{n_{ij}})])$, where x_i is the molar fraction of component i with $x_i > 0.5$ for an extremum of $\Delta_{mix}H_m = f(x_i)$ and the parameters (n_{ij}) deduced from the experimental data of the limiting binary systems are reported in Table 3.

TABLE 2

Experimental values of the enthalpy of formation at the crossing points (A, B, C, . . .) of the quasi-binary sections. The two last columns list the mean values of the enthalpy of formation ($\Delta_{mix}H_{m,mean}$ in kJ mol^{-1} and $\Delta = (\Delta_{mix}H_{m,exp} - \Delta_{mix}H_{m,mean})/\Delta_{mix}H_{m,mean}$)

Points	Coordinates	$\Delta_{mix}H_m$ (kJ mol^{-1})	Mean value	Δ
A	$x_{Cd}/x_{Ga} = 1/3$; $x_{Zn} = 0.692$	1.677	1.821	0.16
	$x_{Ga}/x_{Zn} = 1/3$; $x_{Cd} = 0.077$	1.965		
B	$x_{Cd}/x_{Ga} = 1/1$; $x_{Zn} = 0.60$	2.244	2.353	0.11
	$x_{Ga}/x_{Zn} = 1/3$; $x_{Cd} = 0.20$	2.461		
C	$x_{Cd}/x_{Ga} = 3/1$; $x_{Zn} = 0.429$	2.673	2.712	0.03
	$x_{Ga}/x_{Zn} = 1/3$; $x_{Cd} = 0.429$	2.750		
D	$x_{Cd}/x_{Ga} = 1/3$; $x_{Zn} = 0.429$	2.336	2.412	0.06
	$x_{Ga}/x_{Zn} = 1/1$; $x_{Cd} = 0.142$	2.488		
E	$x_{Cd}/x_{Ga} = 1/1$; $x_{Zn} = 0.333$	2.830	2.882	0.04
	$x_{Ga}/x_{Zn} = 1/1$; $x_{Cd} = 0.333$	2.934		
F	$x_{Cd}/x_{Ga} = 3/1$; $x_{Zn} = 0.20$	2.642	2.641	0.008
	$x_{Ga}/x_{Zn} = 1/1$; $x_{Cd} = 0.60$	2.640		
G	$x_{Cd}/x_{Ga} = 1/3$; $x_{Zn} = 0.20$	2.405	2.357	0.04
	$x_{Ga}/x_{Zn} = 3/1$; $x_{Cd} = 0.20$	2.501		
H	$x_{Cd}/x_{Ga} = 1/1$; $x_{Zn} = 0.143$	2.810	2.874	0.04
	$x_{Ga}/x_{Zn} = 3/1$; $x_{Cd} = 0.428$	2.938		
I	$x_{Cd}/x_{Ga} = 3/1$; $x_{Zn} = 0.077$	2.356	2.308	0.04
	$x_{Ga}/x_{Zn} = 3/1$; $x_{Cd} = 0.692$	2.260		

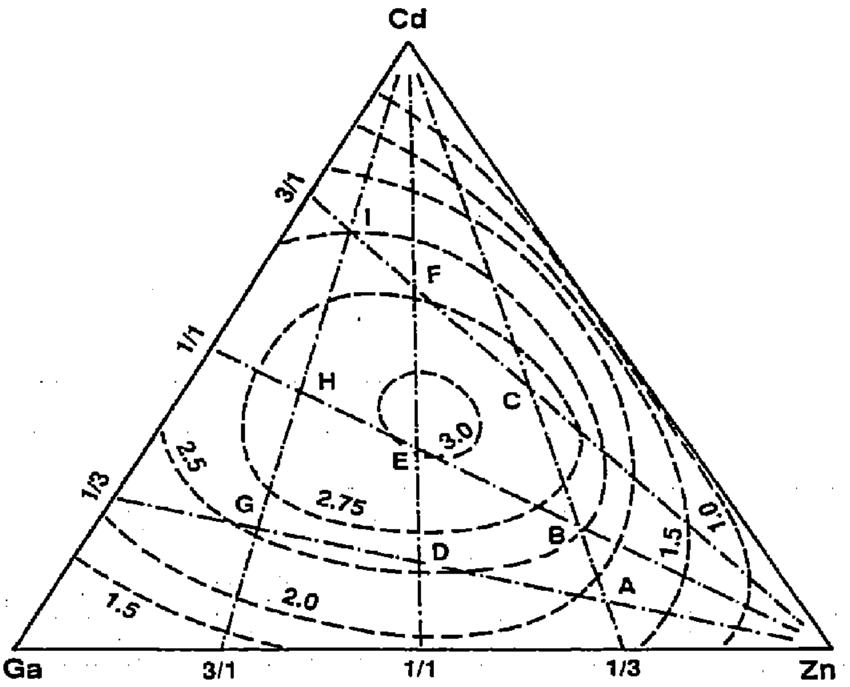

Fig. 3. Isoenthalpic lines (+3.0, +2.75, 2.5, 2.0 and 1.5 kJ mol^{-1}) at 730 K.

TABLE 3

Parameters obtained from the enthalpy data of the limiting binary systems and used in the Hoch–Arphshofen calculation

System	Ref.	x	n	W (J mol^{-1})	W (kK)	±
Cd–Ga	6	Ga	2	5564.0	0.6693	339.4
Cd–Zn	8	Zn	2	4275.9	0.5143	88.8
Ga–Zn	9	Zn	3	1640.9	0.1974	94.2

The surrounded atom model [18] (Mathieu's model)

The surrounded atom model proposed by Brion et al. was extended to ternary [18], quaternary, quinary [2],... alloys. To calculate the molar enthalpy of formation of the studied alloys we used the relation

$$\begin{aligned}\Delta_{\text{mix}}H_{\text{m}} = {} & x_i x_j[x_j \Delta_{\text{mix}}H^{\infty}_{i(ij)} + x_i \Delta_{\text{mix}}H^{\infty}_{j(ij)}] \\ & + x_i x_k[x_k \Delta_{\text{mix}}H^{\infty}_{i(ik)} + x_i \Delta_{\text{mix}}H^{\infty}_{k(ik)}] \\ & + x_j x_k[x_k \Delta_{\text{mix}}H^{\infty}_{j(jk)} + x_j \Delta_{\text{mix}}H^{\infty}_{k(jk)}] \\ & + x_i x_j x_k C[\Delta_{\text{mix}}H^{\infty}_{i(ij)} + \Delta_{\text{mix}}H^{\infty}_{j(ij)} + \Delta_{\text{mix}}H^{\infty}_{i(ik)} + \Delta_{\text{mix}}H^{\infty}_{k(ik)} \\ & + \Delta_{\text{mix}}H^{\infty}_{j(jk)} + \Delta_{\text{mix}}H^{\infty}_{k(jk)}]\end{aligned}$$

with $C = [(z-1)(n+1)+z]/(3z-1)$ where z and n are the mean coordinance and the ponderation factor, respectively. The values of the limiting molar partial enthalpies used in this calculation are listed in Table 4.

The enthalpies of formation of the Cd + Ga + Zn liquid system have been calculated from the relations of Kohler, Muggianu, Hoch–Arpshofen and Mathieu. Table 1 allows a comparison between the evaluated and experimental results. All the relations lead to a satisfying prediction of the enthalpy of mixing. However, along the ternary sections investigated, the

TABLE 4

Limiting partial molar enthalpies of mixing of Cd, Ga and Zn (liquid state) in binary liquid alloys (kJ mol^{-1}) deduced from eqns. (1)–(3)

Cd–Ga		Cd–Zn		Ga–Zn	
$\Delta_{\text{mix}}H^{\infty}$(Cd in Ga)	15.82	$\Delta_{\text{mix}}H^{\infty}$(Cd in Zn)	9.22	$\Delta_{\text{mix}}H^{\infty}$(Ga in Zn)	9.35
$\Delta_{\text{mix}}H^{\infty}$(Ga in Cd)	9.83	$\Delta_{\text{mix}}H^{\infty}$(Zn in Cd)	8.80	$\Delta_{\text{mix}}H^{\infty}$(Zn in Ga)	5.79

best fit between experimental and calculated data is obtained with Kohler's relation.

CONCLUSION

For *n*-component liquid alloys in which the interactions between atoms are weak, the excess molar functions of formation can be correctly predicted by several relations. Essentially the choice of a relation depends to the nature (partial or integral molar values) of the binary data available. In the case of the Cd + Ga + Zn liquid system, the Kohler relation seems to provide the best prediction of the excess molar functions of formation.

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