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Excess thermodynamic functions in the liquid system (Bi–Cd–Ga–In–Pb–Sn–Zn). Measurements and calculations

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Abstract

We summarize our measurements and calculations of enthalpy of mixing and activity in the seven component liquid system (Bi–Cd–Ga–In–Pb–Sn–Zn). The enthalpy measurements were carried out at 700–1000 K using a Calvet type calorimeter. The activity measurements were carried out at 714, 805 and 877 K using an EMF cell with a KCl–LiCl eutectic electrolyte. The calculations were done using the Hoch–Arpshofen model. In the measurements of the partial enthalpy of mixing and activity data, the calculated uncertainties were larger than the difference between the measured and calculated values. For the enthalpy of mixing data in the seven-component system, we needed 21 binary interaction parameters, and for the activity measurements in the five-component (Bi–Cd–Pb–Sn–Zn) system, 20 binary interaction parameters are required. Thus it is possible to calculate large systems, make a few experiments to check the calculations, and thus to be able to help different industries. © 2001 Published by Elsevier Science B.V.

Keywords: Calorimetry; Modeling; Multicomponent systems

1. Introduction

The aim of this research is to show that using a relatively simple model, with only binary interaction parameters, enthalpy of mixing and activity data for large systems can be calculated, which agree with experimental results.

2. The Hoch–Arpshofen model

In an earlier paper, Hoch and Arpshofen [1] derived a model for binary solutions and in a subsequent paper, Hoch [2] derived the model for ternary, quaternary, and larger systems. The binary model is merely a special case of the ternary model. The model is an extension of Guggenheim's [3] treatment of solutions, combined with an adaptation of Pauling's [4] ideas of the metallic bond.

Guggenheim [3], when treating regular solutions and superlattices, speaks of 'treatment of quadruplets of sites, forming regular tetrahedra' and 'triplets of sites, forming equilateral triangles.' Guggenheim [3], however, always treats the strength of the A–B bond in the same way, regardless of what other atoms are present in the complex. In our model, the strength of the A–B bond depends on the number of B atoms to which the A atom bonds, or vice versa. In Pauling's [4] description of a metallic bond, the bond number is defined as the number of bonding electrons divided by the number of neighbors to which the specific atom bonds. In metallic copper, which consists of one bonding electron and 12 neighbors, the bond number is 1/12. This is a one-electron bond, which moves from one neighbor to another. In our model this idea is applied to ionic materials (ceramic) and van der Waals-type forces, in both an attractive and a repulsive mode. This idea is not extravagant because all bonds are caused by the behavior of electrons.

In a multicomponent system with the components A, B, C, D, etc. and their mol fractions x, y, z, u, etc., the effect of the mixing function Fm (Hm, enthalpy of mixing, Sm^{ex}, excess entropy of mixing) of the binary system A–B (mol fractions x and y) in the multicomponent is

$$Fm = Wnx[1-(1-y)^{\{n-1\}}] \quad (1)$$

W is the interaction parameter and n, the size of the complex, is an integer (2, 3, 4, etc.).

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The partial quantities are

$$F_x = Wn[1 - (1-y)^{\{n-1\}} - xy(n-1)(1-y)^{\{n-2\}}] \quad (1a)$$

$$F_y = Wnx(n-1)(1-y)^{\{n-1\}} \quad (1b)$$

$$F_z = H_u = -Wnxy(n-1)(1-y)^{\{n-2\}} \quad (1c)$$

In the multicomponent system (A–B–C–D–etc.), the other binary systems (A–C, A–D, A–etc., B–C, B–D, B–etc., C–D, C–etc., and D–etc.) contribute similarly to the thermodynamic properties of the multicomponent system.

The above equations also apply to the binary system A–B; if one replaces y by $(1-x)$ then $x+y=1$ and $z=u=\ldots=0$, in binary systems

$$Fm = Wn[x - x^n] \quad (2)$$

$$Fx = Wn[1 - nx^{\{n-1\}} + (n-1)x^n] \quad (2a)$$

$$Fy = Wn(n-1)x^n \quad (2b)$$

In the binary system A–B, the mol fraction of the component is x so that in Eq. (2), Fm is maximum (positive or negative) at $x>0.5$.

In our nomenclature 3,(A) means that n is equal to 3, and x is the mol fraction of A.

The partial quantities represented by Eq. (2) do not change sign when the composition changes from $x=0$ to $x=1$; the sign of Fx and Fy are determined by the sign of W.

Sm^{ex} the excess entropy of mixing has also the same form as Eq. (2), but it can have another value for n, and x can be the mol fraction of the other component, thus it is possible that

$$Sm^{\mathrm{ex}} = Ur(y - y^r) \quad (3)$$

where U is the entropy constant, again independent of composition.

The excess Gibbs energy of mixing, Gm^{ex}, is a combination of Hm and Sm^{ex}. Eq. (2) can be applied to Gm^{ex} only if Sm^{ex} has the same n and x as Hm, or if Sm^{ex} is zero.

It is possible that in a binary system on one side attractive, on the other repulsive forces are present (as in Au–Si, CaO–SiO_2). In this case two terms of Eq. (1) are needed:

$$Fm = W_1xn[1 - (1-y)^{\{n-1\}}] + W_2ym[1 - (1-x)^{\{m-1\}}] \quad (4a)$$

or

$$Fm = W_1xn[1 - (1-y)^{\{n-1\}}] + W_2xm[1 - (1-y)^{\{m-1\}}] \quad (4b)$$

and

$$W_1 > 0 \text{ and } W_2 < 0 \text{ or vice versa} \quad (4c)$$

Though we talk about ‘complexes’, the ideal Gibbs energy of mixing is, as in Guggenheim [3]

$$Gm^{\mathrm{id}} = RT(x_1 \ln x_1 + x_2 \ln x_2 + x_3 \ln x_3 + \ldots) \quad (5)$$

A great advantage of our model is that we have never needed ternary interaction parameters. More important, we can obtain the binary interaction parameters from ternary or quaternary data by regression analysis; the latter must agree with data obtained from binary data.

The interaction parameters are designated depending on what experimental data they were calculated from: Wh from Hm enthalpy of mixing, Ws from Sm^{ex}, excess entropy of mixing, and Wg from Gm^{ex}, excess Gibbs energy of mixing.

In all of our calculations, the thermodynamic quantities are divided by R, the gas constant. Thus the enthalpy H and the Gibbs energy G are expressed in kK (kiloKelvin); the entropy S and the heat capacity Cp are dimensionless.

The model always mixes metal atoms or cations, i.e. B_2O_3 is always treated as $BO_{1.5}$ and Na_2O as $NaO_{0.5}$. This obviously requires a change in composition before the model can be applied.

In binary systems, which follow Eq. (1), the maximum (positive or negative) of Gm is at $x=(n-1)/n$, and of Hm at $x=(1/n)^{(1/(n-1))}$.

3. Results

Table 1 shows the interaction parameters evaluated from various sources [5–12]. In the enthalpy of mixing measurements, we added one component to the equimolar composition of the others. Thus depending on how many sets using different added components are measured, we can obtain a good picture of the large system.

Ptak et al. [13] measured the zinc activity in the liquid quinary system Bi–Cd–Pb–Sn–Zn at 127 compositions and 714, 805, 877 K. Hoch and Moser [14] calculated the activity coefficients of Zn at the same compositions and temperatures, using the binary interaction coefficients given in Table 1. The average of the measured and calculated activity coefficients, $T \ln Y$ are given in Table 2, together with the uncertainty in the calculated values, the difference and absolute difference between measured and calculated values. The agreement is excellent: the differences are smaller than the uncertainty in the calculated values.

The enthalpy of mixing in the liquid quinary system Cd–Ga–In–Sn–Zn was measured by Perona-Silhol et al. [15], and is shown in Fig. 1. We only present the data with Cd and Zn additions to keep the figure clear. The vertical line is the uncertainty in the calculated values. The agreement is good.

Ouédraogo et al. [16] measured the enthalpy of mixing in the six-component system Bi–Cd–Ga–In–Sn–Zn. Fig.

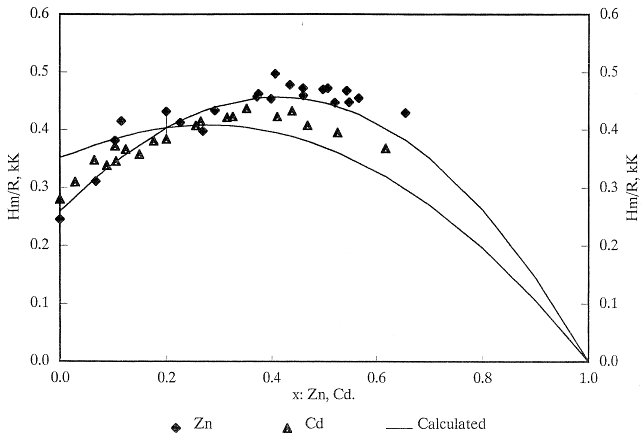
Table 1
Interaction parameters in the seven-component liquid system Bi–Cd–In–Pb–Sn–Zn

Binary system	*n*	*x*	*Wh* (kK)	±	*n*	*x*	*Ws* (kK)	±	Reference
Bi–Cd	4	Cd	0.063	0.009	4	Cd	0.103	0.009	[5]
Bi–Ga	3	Ga	0.242	0.021					[6]
Bi–In	2	Bi	−0.418	0.038					[5]
Bi–Pb	2	Bi	−0.239	0.002	2	Bi	0.052	0.051	[5]
Bi–Sn	2	Bi	0.025	0.010	4	Sn	−0.019	0.023	[5]
Bi–Zn	3	Zn	0.487	0.028	3	Zn	0.223	0.080	[5–7]
Cd–Ga	2	Cd	0.695	0.054					[8]
Cd–In	3	Cd	0.157	0.012					[5]
Cd–Pb	2	Pb	0.298	0.078	2	Pb	0.082	0.025	[5]
Cd–Sn	3	Cd	0.203	0.018	3	Cd	0.132	0.029	[5]
Cd–Zn	2	Cd	0.514	0.011	2	Cd	0		[5]
Ga–In	2	Ga	0.274	0.008					[9]
Ga–Pb	2	Pb	0.824	0.069					[10]
Ga–Sn	2	Sn	0.210	0.008					[11]
Ga–Zn	3	Zn	0.176	0.010					[12]
In–Pb	2	Pb	0.228	0.001					[10]
In–Sn	2	Sn	−0.049	0.003					[5]
In–Zn	3	Zn	0.358	0.027					[5]
Pb–Sn	2	Sn	0.338	0.032					[5]
Pb–Zn	3	Zn	0.750	0.060	3	Zn	0		[5]
Sn–Zn	3	Zn	0.364	0.020	3	Zn	0.234	0.063	[5]

Table 2
Summary of the data for the Zn activity in the five-component liquid system Bi–Cd–Pb–Sn–Zn

T (kK)	*T* ln *Y* Zn (kK)		Measured − calculated (kK)	Absolute (measured − calculated) (kK)
	Measured	Calculated		
0.714	0.841	0.863±0.093	−0.022	0.084
0.805	0.805	0.830±0.100	−0.025	0.084
0.877	0.780	0.805±0.105	−0.025	0.084

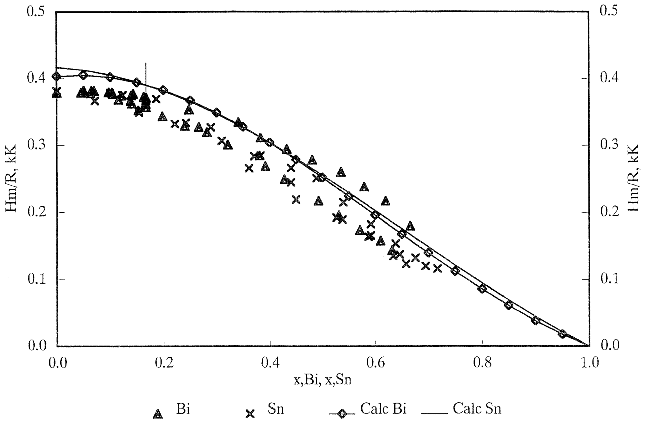
2 shows the integral enthalpy of mixing adding Bi with respect to Sn to the equimolar mixture of the other components. The agreement is very good, keeping in mind that in the measurements small errors add up.



vertical line: calculated uncertainty ±

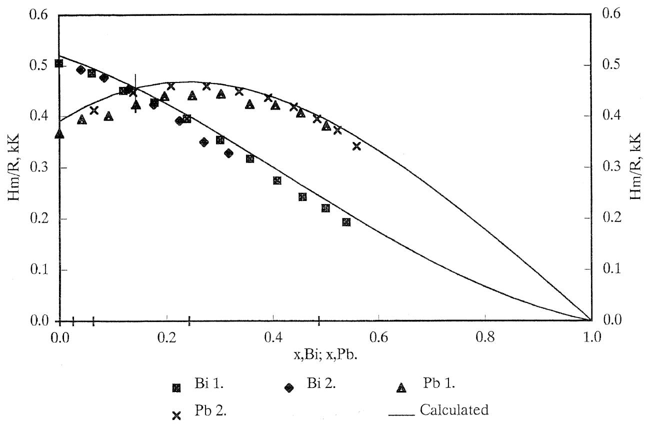
Fig. 1. Enthalpy of mixing in the five-component system Cd–Ga–In–Sn–Zn along the line connecting Zn with respect to Cd and the center of gravity of the other four components.

In Fig. 3 we show the enthalpy of mixing in the seven-component system (Bi–Cd–Ga–In–Pb–Sn–Zn) of Gambino et al. [17]. The agreement between measured and calculated values is very good. Fig. 4 shows the partial



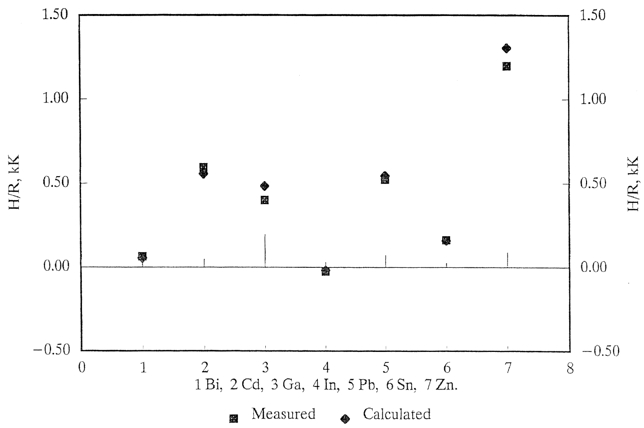
Vertical line: calculated uncertainty ±
Sn 3 sets of measurements, Bi 8 sets of measurements.

Fig. 2. Integral enthalpy of mixing in the liquid six-component system Bi–Cd–Ga–In–Sn–Zn along the line connecting Bi with respect to Sn and the center of gravity of the other components.



vertical line uncertainty ±. Bi and Pb two set of measurements, 1 and 2.
H partial from partial enthalpy measurements in Table III.

Fig. 3. Enthalpy of mixing in the liquid seven-component system Bi–Cd–Ga–In–Pb–Sn–Zn along the line connecting Bi with respect to Pb and the center of gravity of the six components.



Vertical line: total uncertainty ±.
Uncertainty much larger than difference between measured and calculated values.

Fig. 4. Partial enthalpies in the liquid Bi–Cd–Ga–In–Pb–Sn–Zn system at the center of gravity of the components; $x=0.143$.

enthalpy of mixing at $x=0.143$ calculated from the partial enthalpies given in Table 4.

Table 3 presents the partial enthalpies of mixing in the seven-component system Bi–Cd–Ga–In–Pb–Sn–Zn. The composition is in the center of the system, for each component $x=1/7=0.143$. Each value was measured four times, except Ga which was measured only twice. The agreement between measured and calculated values is good. The data are also shown in Fig. 4. In this figure, the vertical lines starting at zero, are the combined uncertainty (measured + calculated) $(x_1^2+x_2^2)^{0.5}$.

To show the accuracy of the enthalpy of mixing measurements, Table 4 shows the enthalpy of mixing for a quaternary, quinary, six- and seven-component system at the equal molar composition, starting with the addition of two different components. The first column contains the system, the second the equimolar composition, the third the added component, the fourth the enthalpy of mixing obtained and the fifth the uncertainty between the two measured values. In the seven-component system, we also calculated the enthalpy of mixing from the measured and calculated partial enthalpies of mixing, each with its uncertainty. In each case the data agree well.

4. Conclusions

The model used in this publication accounts correctly for the variation of the enthalpy of formation of multi-component metallic alloys. It has to be emphasized that the experimental and calculated partial quantities agree very well. With low melting alloys it is quite difficult to carry out direct drop calorimetry, and in these cases calculated values are more reliable than experimental ones. The model used in the present calculations permits a correct estimation of thermodynamic quantities for a system with q components. Reliable experimental values are increas-

Table 3
Partial enthalpy of mixing of the components in the seven-component system Bi–Cd–In–Pb–Sn–Zn at $x=0.143$[a]

Component	Partial enthalpy (kK)		
	Measured	Calculated	Measured − calculated
Bi	0.0627±0.0038	0.0534±0.0293	0.0094
Cd	0.5932±0.0349	0.5562±0.0305	0.0369
Ga	0.4006±0.1925	0.4830±0.0261	−0.0834
In	−0.0252±0.0141	−0.0183±0.0244	−0.0068
Pb	0.5229±0.0140	0.5449±0.0683	−0.0220
Sn	0.1623±0.0104	0.1595±0.0216	0.0028
Zn	1.1952±0.0368	1.3011±0.0781	−0.1059
Integral enthalpy of mixing			
*H*mix	0.4160±0.0438	0.4401±0.0397	

[a] Four experiments each, except for Ga with only two experiments.

Table 4
Enthalpy of formation of *m*-component liquid alloys at the equal molar fraction composition

System	x		ΔHmix (kK)
Bi–Cd–Ga–Zn	0.25	Bi additions	0.412
		Cd additions	0.431±0.010
Bi–Cd–Ga–In–Zn	0.20	Bi additions	0.388
		In additions	0.375±0.007
Bi–Cd–Ga–In–Sn–Zn	0.167	Bi additions	0.361
		Sn additions	0.363±0.001
Bi–Cd–Ga–In–Pb–Sn–Zn	0.143	Bi additions	0.443
		Pb additions	0.435±0.004
From measured partial enthalpies			0.416±0.029
From calculated partial enthalpies			0.440±0.017

ingly more difficult to obtain as q, the number of components, increases.

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