Thermochimica Acta, 122 (1987) 395–401
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMODYNAMICS OF THE LIQUID ALUMINUM–GALLIUM–TIN SYSTEM

MICHAEL HOCH

Department of Materials Science and Engineering, University of Cincinnati, Cincinnati, OH 45221-0012 (U.S.A.)

(Received 14 April 1987)

ABSTRACT

The thermodynamic data, enthalpy of mixing and partial Gibbs energy of aluminum in the liquid aluminum–gallium–tin system were analyzed by the Hoch–Arpshofen model. It is shown that the binary systems are quite simple, and no ternary interaction coefficients are needed to represent the ternary data.

INTRODUCTION

In an earlier paper [1], the Hoch–Arpshofen model was extended for ternary and larger systems; the original derivation [2] was for binary systems only.

Let a solution contain components (A, B, C, D, ...) with the mole fractions (x, y, z, u, ...). Then the contribution of the A–B binary system to the solution is [1]

$$H_{\mathrm{m}} = Wnx\left[1 - (1-y)^{(n-1)}\right] \tag{1}$$

$$\overline{H}_x = Wn\left[1 - (1-y)^{(n-1)} - xy(n-1)(1-y)^{(n-2)}\right] \tag{2}$$

$$\overline{H}_y = Wnx(n-1)(1-y)^{(n-1)} \tag{3}$$

$$\overline{H}_z = \overline{H}_u = -Wnxy(n-1)(1-y)^{(n-2)} \tag{4}$$

where H_{m} is the enthalpy of mixing and $\overline{H}_x$, etc. are the partial quantities. W is the interaction parameter and n is an integer (2, 3, 4, etc.). The values of n and W are deduced from the binary system: if we make $x + y = 1$, we recover the equations for the binary system [2]

$$H_{\mathrm{m}} = Wn(x - x^n) \tag{5}$$

$$\overline{H}_x = Wn\left[1 - nx^{(n-1)} + (n-1)x^n\right] \tag{6}$$

$$\overline{H}_y = Wn(n-1)x^n \tag{7}$$

The quantity x is the mole fraction of the component, so that the maximum of H_m (either positive or negative) is at $x > 0.5$. The quantity n is chosen such that W, determined from thermodynamic data, is independent of composition. From each experimental point one value of W is obtained; all of these can be averaged and a standard deviation obtained.

$S_{m,ex}$, the excess entropy of mixing, has the same form as eqn. (5), but it can have another value for n, and its maximum may be at $x < 0.5$. Thus it is possible that

$$S_{m,ex} = rU(y - y^r) \tag{8}$$

where U is a constant.

$G_{m,ex}$, the excess Gibbs energy of mixing, which is a combination of H_m and $S_{m,ex}$, will have a simple form only if $S_{m,ex}$ has the same form as H_m or is zero.

The partial quantities represented by eqns. (3) and (4) do not change sign when the composition changes from $x = 0$ to $x = 1$; the signs of $\overline{H}_x$ and $\overline{H}_y$ are determined by the sign of W. In other words, one interaction parameter W describes one type of interaction or reaction in a system. If two reactions exist in a binary system, then two interaction parameters, an attractive W and a repulsive M, are needed. Each has its major effect at different compositions with different dependencies on composition (n and x in one case, m and y in the other). Thus

$$H_m = nW(x - x^n) + mM(y - y^m) \tag{9}$$

W and M are determined by least-square analysis; confidence limit and error in W and M are also calculated. The values of n and m are varied until the confidence limit is high and the error limits on W and M reach the smallest ratio of error of value. A relationship seems to exist between n and m: $n = 2m$, or $m = 2n$.

The ideal Gibbs energy of mixing is always

$$G_{m,id} = RT(x \ln x + y \ln y + z \ln z + \ldots) \tag{10}$$

The other binary systems (A–C, A–D, B–C, etc.) contribute similarly to the thermodynamic properties of the solution.

The advantage of the present method is that in a binary system, a maximum of only four interaction parameters is needed: two for H_m, the enthalpy of mixing, and two for $S_{m,ex}$, the excess entropy of mixing. No ternary or larger system has yet been found in which ternary or larger interaction parameters are needed.

In this research the ternary system aluminum–gallium–tin was investigated. Detailed enthalpy of mixing and partial Gibbs energy measurements of aluminum at 1023 K were published by Gaune et al. [3]. They also used higher order polynomials to represent mathematically H_m, the enthalpy of mixing, and $S_{m,ex}$, the excess entropy of mixing, in the bounding binary

TABLE 1

Enthalpy of mixing in the liquid Al–Ga–Sn system

		Binaries		Regression analysis	
		W_h (kK)	±	W_h (kK)	±
Sn–Al	3,(Al)	0.5446	0.0594	0.5574	0.0062
Sn–Ga	2,(Sn)	0.2100	0.0082	0.1220	0.0183
Al–Ga	3,(Al)	0.0727	0.0228	0.0416	0.0086
R				0.9988	

x,Sn	x,Al/x,Ga	H_m (cal mol^{-1})			
		Measured (ref. 3)	Calculated	±	Meas. − calc.
		582.3	584.7	58.9	−2.4
0.0	1/3	105.0	101.6	31.9	3.4
0.1		244.1	282.4	31.3	−38.3
0.2		366.7	406.7	34.5	−40.0
0.3		455.3	479.9	36.9	−24.6
0.4		498.8	507.2	37.3	−8.4
0.5		492.5	493.8	35.3	−1.3
0.6		438.4	445.0	31.1	−6.6
0.0	1/2	125.0	128.5	40.3	−3.5
0.1		349.0	344.4	39.8	4.6
0.2		495.0	491.1	44.4	3.9
0.3		573.0	575.5	48.1	−2.5
0.4		592.0	604.6	48.8	−12.6
0.5		561.0	585.0	46.3	−24.0
0.6		491.0	523.8	40.9	−32.8
0.0	1/1	157.0	162.6	51.0	−5.6
0.1		425.5	451.2	52.3	−25.7
0.2		611.5	645.2	61.8	−33.7
0.3		724.7	754.7	69.0	−30.0
0.4		770.5	789.8	71.2	−19.3
0.5		755.6	760.4	68.2	−4.8
0.6		688.9	676.7	60.4	12.2
0.7		569.8	548.8	48.8	21.0
0.0	2/1	153.0	160.6	50.4	−7.6
0.1		516.1	527.8	58.0	−11.7
0.2		766.9	774.7	75.8	−7.8
0.3		916.2	914.5	88.3	1.7
0.4		974.3	960.3	92.8	14.0
0.5		951.9	925.3	89.6	26.6
0.0	3/1	135.0	142.3	44.6	−7.3
0.1		557.0	552.0	58.4	5.0
0.2		856.0	828.2	81.9	27.8
0.3		1021.0	985.7	97.5	35.3
0.4		1078.0	1039.2	103.4	38.8
0.5		1040.0	1003.3	100.3	36.7
0.6		926.0	892.9	89.6	33.1

TABLE 2

Partial Gibbs energy of aluminum at 1023 K in liquid Al–Ga–Sn alloys

		Binaries						Regression analysis	
		W_h (kK)	±	W_s	±	W_g (kK) 1.023	±	W_g (kK) 1.023	±
Al–Ga	3,(Al)	0.0727	0.0288	0.0373	0.0060	0.0345	0.0294	0.0520	0.0289
Al–Sn	3,(Al)	0.5446	0.0594	0.2280	0.0810	0.3114	0.1020	0.3411	0.0169
Ga–Sn	2,(Sn)	0.2100	0.0080	0.0629		0.1457	0.0080	0.8182	0.2264
R								0.9906	

x,Al	x,Ga/x,Sn	$RT \ln a(\text{Al})$ (cal mol^{-1})			
		Measured (ref. 3)	Calculated	±	Meas. − calc.
		−1556	−1440	248	−116
0.1	1/9	−2812	−2959	568	147
0.2		−1793	−1718	512	−75
0.3		−1200	−1111	440	−89
0.4		−885	−772	359	−113
0.5		−653	−576	274	−77

0.6		−486	−457	191	−29
0.1	4/1	−4243	−4021	238	−222
0.3		−2163	−2008	163	−155
0.5		−1258	−1164	93	−94
0.7		−681	−629	37	−52
0.9		−233	−203	5	−30
0.2	1/1	−2488	−2242	344	−246
0.4		−1347	−1209	216	−138
0.14		−3325	−2853	384	−472
0.33		−1750	−1472	260	−278
0.6		−791	−715	106	−76
0.8		−346	−365	29	19
		(ref. 6)			
0.34	2.43	−1019	−1683	176	664
0.2	0.33	−2954	−1897	456	−1057
0.34	0.41	−1520	−1179	336	−341
0.2	3.00	−2237	−2638	222	401
		−1933	−1849	297	−83

systems. For the ternary system, they used Toop's [5] model with three ternary constants. As will be shown, a much simpler representation, using our model, gives better results.

METHOD OF CALCULATION

In our treatment of binary systems, all thermodynamic values are divided by R, the gas constant. Thus H_m (the enthalpy of mixing) and G_m (the Gibbs energy of mixing) are expressed in kK (kiloKelvin), S (the entropy) and Cp (the heat capacity) are dimensionless.

In calculating ternary systems, the top of the tables contain the binary terms expressed as above, but in the tables, where comparisons with experimental data are made, the values are converted to the units given in the experimental paper (cal, kcal, J, kJ, etc.). The top of the tables also contain binary coefficients calculated by regression analysis from the ternary data (if enough experimental data are available). In the ternary tables, at the heads of the columns for measured, calculated, $\pm$, and measured − calculated values, an average of the values in each column is given, which permits a rapid overview of the agreement between calculated and measured values.

We use the following nomenclature: if W was derived from the enthalpy of mixing values, it is designated by W_h. If two interaction parameters are needed to describe H_m in a system, the second value is designated by M_h. For the excess entropy of mixing we use the notation W_s. In the rare cases where $S_{m,ex}$ has the same form as $G_{m,ex}$ or is 0, we can use W_g for $G_{m,ex}$ (the excess Gibbs energy). The notation 4,(Cu) indicates that in that system $n = 4$, and x is the mole fraction of copper, to which a value of W_h or W_s then belongs.

In all the treatments of binary data an average value and a standard deviation $\pm$ are given when one constant is calculated. When least-square analysis is used to determine two constants, an error $\pm$ is given for each, plus the regression coefficient R. In addition to these uncertainties, caused by fitting the model to the experimental data, an additional uncertainty exists for the $\pm$ value given by Hultgren et al. [3]: where Hultgren's values are used these values are converted to our model at $x = 0.5$. This uncertainty, which is generally larger than that caused by fitting the model, is added to the first value (generally W_h) by $c = (a^2 + b^2)^{1/2}$, and introduced into the tables describing ternary systems.

Enthalpies of mixing values were treated according to eqns. (5), (6) and (7). To obtain the excess entropy of mixing ($S_{m,ex}$) two procedures were applied: W_h was calculated from H_m, and with this value and $G_{m,ex}$ we calculated $TS_{m,ex}$ at every composition

$$TS_{m,ex} = W_h(n, x) - G_{m,ex} \tag{11}$$

From this value we obtained W_s, using eqns. (5)–(7). The other method which we also applied at every composition, decomposes $G_{m,ex}$ into its components by least-squares analysis

$$G_{m,ex} = W_h(n, x) - TW_s(r, y) \tag{12}$$

The values n and r are varied until the error in W_h and W_s is minimal and the regression coefficient R is maximal. Obviously, if $S_{m,ex}$ has the same shape of H_m this method is not applicable.

In binary systems we never calculate W_g; but when calculating in a ternary system, W_g can be used: e.g., $-TW_s = W_g$.

RESULTS

The thermodynamic data of Hultgren et al. [4] were used to evaluate W_h and W_s of the Al–Ga and Al–Sn systems. In both cases, W_h and W_s were of the same form 3,(Al), making W_g also 3,(Al). The error limits contain the uncertainties given by Hultgren. For the system Ga–Sn, the equation given by Gaune et al. [4] for H_m was evaluated between x,Al 0.1 and 0.9. It turned out that a regular solution ($n = 2$) is good. For $S_{m,ex}$ Gaune et al. [3] give a regular model representation.

The enthalpy of mixing data are given in Table 1. The agreement between measured and calculated values is excellent. Averaging the square of the difference between measured and calculated values gives a deviation of 21.6 cal mol^{-1}, which is smaller than the value of 26 cal mol^{-1} obtained by Gaune et al. [3]. The binary constants calculated by regression analysis from the ternary data are in good agreement with the binary data.

The partial Gibbs energy of aluminum is calculated in Table 2 and compared with the measured values of Gaune et al. [3] and Lee and Yazawa [6]. The agreement with the values of Gaune is good; with those of Lee and Yazawa moderate. The binary Ga–Sn constant calculated by regression analysis (only data of Gaune et al.) is obviously wrong. It also has a large error limit: this is due to the fact that this constant contributes very little to the partial Gibbs energy of aluminum.

REFERENCES

1 M. Hoch, Calphad, 11 (1987) 219.
2 M. Hoch and I. Arpshofen, Z. Metalldke., 75 (1984) 23.
3 J.L. Gaune, M. Gambino, J.-P. Bros, R. Martin-Garin and I. Ansara, Thermochim. Acta, 18 (1977) 217.
4 R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser and K.K. Kelley, Selected Values of Thermodynamic Properties of Binary Alloys, ASM Metals Park, OH, 1973.
5 W.G. Toop, Trans. Met. Soc. AIME, 233 (1965) 850.
6 Y.K. Lee and A. Yazawa, J. Jpn. Inst. Met., 33 (1969) 323; Y.K. Lee, Nippon Kinzoku Gakkaishi, 4 (1970) 9.