

# Partial Heats of Mixing in the Bi-Sn System

R. L. SHARKEY AND M. J. POOL

Partial heats of mixing have been measured at 725 K for liquid Bi-Sn alloys using a liquid metal solution calorimeter. Integral heats of mixing were calculated and were found to be endothermic. The experimental data are analyzed using the subregular model and the modified quasichemical model.

IN a previous paper<sup>1</sup> a model was proposed for describing heat of mixing curves for binary solid and liquid alloys. The proposed model was applied to 84 binary systems, with the Bi-Sn system being one of the systems not fitting the model. The Bi-Sn data used in the calculations were taken from Hultgren *et al.*<sup>2</sup> They are based on electromotive force measurements of Seltz and Dunkerley<sup>3</sup> (608 K) and supported by the direct calorimetric measurements of Huber<sup>2</sup> (748 K). These heats of mixing are endothermic, being in the range 0 to 25 cal per g-atom at 608 K. However, older investigations based on calorimetric measurements by Magnus and Mannheim<sup>4</sup> (600 K) and Kawakami<sup>5</sup> (623 K) result in exothermic heats of mixing in the range 0 to -160 cal per g-atom. Because of the discrepancies between these investigations and the availability of equipment capable of direct measurement of partial heats of mixing, a reinvestigation of this system by solution calorimetry was undertaken.

## EXPERIMENTAL PROCEDURE

The liquid metal solution calorimeter used in this work is of the twin-well type operated in a differential mode. It is similar in design to other differential twin-well calorimeters described in the literature<sup>6,7</sup> and is completely described by Sharkey.<sup>8</sup> Two identical calorimeter wells are located symmetrically within a 12-in. diam aluminum block. Each well contains a multijunction thermopile composed of 96 chromel-alumel thermocouples. Forty-eight of these couples lie adjacent to a stainless steel tube which contains the solvent bath. The remaining 48 couples are adjacent to the aluminum block. This crucible-thermopile arrangement is very similar to that described by Kleppa.<sup>6</sup>

The two thermopiles are connected in series so that the electromotive force output from one opposes the electromotive force output from the other. The measured electromotive force difference is thus indicative of the temperature difference between two identical solvent baths. The differential output of the thermopiles is fed into a Leeds and Northrup dc microvolt amplifier and the amplifier output is the input signal for a Leeds and Northrup millivolt strip chart recorder. The thermopile output is stable to  $\pm 0.25 \mu\text{V}$  over a 10 hr time period.

R. L. SHARKEY, formerly Graduate Student, Department of Materials Science and Metallurgical Engineering, University of Cincinnati, Cincinnati, Ohio, is now Research Metallurgist, American Steel Foundries, East Chicago, Ind. M. J. POOL is Associate Professor of Materials Science, Department of Materials Science and Metallurgical Engineering, University of Cincinnati.

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The aluminum calorimeter block is maintained under vacuum within a plain carbon steel tank which is sealed by stainless steel "O" rings. The vacuum tank is situated in a larger steel cylinder which is used as the core of the furnace. Temperature is maintained by four kanthal wire resistance elements; one each above and below the vacuum chamber and two side elements on the core cylinder. Power is supplied to the top and bottom coils by 120 v Powerstats, to one side coil by a 240 v Powerstat, and to the second side coil by a Bayley Instruments precision temperature controller. The temperature of the system can be varied from 500 to 825 K with a stability of  $\pm 0.25$  K on a 36 hr cycle. There is a long-term decrease of the calorimeter temperature of approximately 2 K in 30 days. This requires periodic adjustment of the precision temperature controller to maintain the desired temperature.

A stainless steel tube ( $\frac{5}{16}$  in. OD) connects the reaction chamber to a stopcock assembly above the calorimeter. A molybdenum stirring paddle is attached to the lower end of this sample drop tube and is submerged in the solvent bath. The tube is dynamically sealed at the top of the calorimeter and is rotated at 10 rpm by a drive motor and gear mechanism located on the lid of the calorimeter. Samples are introduced into a Pyrex solvent crucible in the reaction chamber through this tube.

In the course of approximately 70 experiments in the Bi-Sn system it was found that the time for solution was of the order of 8 min and the post-reaction time (time required to return to equilibrium) was about 50 min. This gives sufficient data to accurately determine the calorimeter heat transfer rate.

Bi-Sn baths of 50 g total weight were made up at compositions of 10 at. pct intervals from pure tin to pure bismuth. The number of g-atoms of total solution ranged from 0.42 for pure tin baths to 0.23 for pure bismuth baths. Baths and samples were prepared from tin stick, 99.9 pct by weight, the principal impurity being antimony, and bismuth shot, 99.999 pct by weight. Molybdenum samples (cut from molybdenum rod, 99.99 pct by weight) were used as standards to calculate the effective reaction cell heat capacity. The Sn, Bi, and Mo sample sizes were approximately 0.0004, 0.0004, and 0.0008 g-atoms, respectively, such that the magnitudes of the  $\Delta\text{emf}$  vs time curves were similar for each.

Samples were dropped into each bath in the order Sn, Mo, Bi. Each molybdenum standard was used to calculate the effective reaction cell heat capacity for the calculation involving the prior tin sample and the following bismuth sample. At the time each sample was added to the bath both the sample temperature and the calorimeter temperature were recorded. These

temperatures were used to calculate the actual sensible heat involved in each measurement. The sensible heats were subtracted from the calorimetric measurements on the bismuth and tin samples in order to determine the partial heats of solution at 725 K. The sensible heats for Bi, Sn, and Mo were determined from heat content data taken from Hultgren *et al.*<sup>2,9</sup>

The bath in the calorimeter was maintained under a pressure of  $10^{-2}$  torr with a mechanical pump. Each bath remained in the calorimeter for 24 hr. Average bath weight losses, taking into account the weights of sample additions, ranged from 0.2 wt pct for tin-rich baths to 0.3 wt pct for bismuth-rich baths. The weight loss is due primarily to the fact that some bath material remains on the stirring paddle when it is removed from the bath. The increase in weight loss for bismuth-rich baths is not enough to significantly alter the average compositions to which the partial heat measurements are referred.

#### ERROR ANALYSIS

The calorimetric measurements were determined using the following equation,

$$\Delta H(\text{calorimeter}) = C(\Delta \text{emf}) + CK\Delta A \quad [1]$$

a derivation of which is given by Pool and Guadagno.<sup>10</sup>  $\Delta H(\text{calorimeter})$  is the sum of the heats resulting from the dissolving process and the sensible heat to bring the sample from the initial temperature to the bath temperature;  $C$  is the reaction cell heat capacity;  $\Delta \text{emf}$  is the differential electromotive force output at time,  $t$ , where  $t$  is some time after the completion of the reaction;  $K$  is the Newtonian cooling constant; and  $\Delta A$  is the area under the electromotive force vs time curve from  $t = 0$  to  $t = t$ .

The main sources for error arise from the reproducibility of the cell heat capacity under given conditions, the reproducibility of the product  $CK$  under given conditions, and the accuracy of the sensible heat for the standard which, if in error, will shift the cell heat capacity value by a constant amount. The error in terms of the variance can be approximated by Eq. [2],

$$\sigma_{\Delta H}^2 \approx [\Delta \text{emf}(\sigma_{C_1})]^2 + [\Delta A(\sigma_{CK})]^2 + [(\Delta \text{emf} + K\Delta A)\sigma_{C_2}]^2 \quad [2]$$

where  $\sigma_{C_1}$  and  $\sigma_{CK}$  are based on the reproducibility of the measurements and  $\sigma_{C_2}$  is based on the error associated with the sensible heat calculation for the molybdenum standard.

The standard error,  $\sigma$ , for both  $C$  and the product  $CK$  was calculated from a least-squares analysis of data obtained from 35 molybdenum standards. Both quantities were assumed to be a linear function of the number of moles of bath solvent. It was found that  $\sigma_{C_1} = 0.00061$  cal per  $\mu\text{v}$  and  $\sigma_{CK} = 0.000126$  cal per  $\mu\text{v}\text{-min}$ . The accuracy of the heat capacity measurement is based on the absolute error stated by Hultgren *et al.*<sup>2</sup> for the sensible heat of molybdenum (298 to 725 K) which is  $\pm 8$  cal per mole. Using this value  $\sigma_{C_2} \approx 0.00019$  cal per  $\mu\text{v}$ . These three values yield standard errors of approximately 43 cal per g-atom for the bismuth samples and 36 cal per g-atom for the tin samples.

Table I. Calorimetric Measurements for Bismuth and Tin at 725K

$X_{\text{Sn}}$ Average	$(\overline{\Delta H}_{\text{Bi}} \pm 43)$ cal per g-atom	$(\overline{\Delta H}_{\text{Sn}} \pm 36)$ cal per g-atom
0.999		8.48
0.998		4.19
0.999	119.21	
0.998	126.14	
0.900		14.98
0.899		2.61
0.898		-25.26
0.900	60.12	
0.898	125.56	
0.898	141.17	
0.800		-3.89
0.800		17.96
0.799		19.35
0.800	95.33	
0.799	64.95	
0.700		69.57
0.700		13.41
0.699		-2.36
0.700	61.29	
0.700	71.23	
0.699	39.46	
0.600		57.86
0.600		16.36
0.600		33.65
0.600	90.02	
0.600	26.23	
0.600	33.44	
0.500		32.63
0.500		20.69
0.500		61.33
0.500	47.62	
0.500	-10.22	
0.500	36.00	
0.401		28.53
0.401		54.95
0.401		110.95
0.401	-17.95	
0.401	58.91	
0.401	12.68	
0.300		110.73
0.301		36.83
0.302		71.12
0.301	6.41	
0.301	16.51	
0.302	22.56	
0.201		118.02
0.202		90.88
0.202		48.51
0.200	-8.41	
0.200	23.48	
0.200	24.06	
0.199	-4.71	
0.101		112.72
0.102		173.53
0.103		84.10
0.100	6.78	
0.100	25.34	
0.100	12.04	
0.000		124.72
0.002		169.34
0.004		162.48
0.002	6.43	
0.003	-25.51	
0.004	9.10	

The error limits on individual measurements are reported as plus or minus the standard error as determined by Eq. [2]. The error limit on the average of several measurements is reported as the error on an individual measurement divided by  $N^{1/2}$  where  $N$  is the

Table II. Partial and Integral Heats of Mixing for Bi-Sn Alloys at 725K

$X_{Sn}$	Partial Heats, cal per g-atom				Integral Heats, cal per g-atom*
	Experimental		Calculated		
	$\overline{\Delta H}_{Bi}$	$\overline{\Delta H}_{Sn}$	$\overline{\Delta H}_{Bi}$	$\overline{\Delta H}_{Sn}$	
1.0	122 ± 30	6 ± 25	124	0	0
0.9	109 ± 25	-3 ± 21	103	1	11
0.8	80 ± 30	11 ± 21	84	5	20
0.7	57 ± 25	27 ± 21	66	11	27
0.6	50 ± 25	36 ± 21	49	20	31
0.5	24 ± 25	38 ± 21	35	31	33
0.4	18 ± 25	65 ± 21	23	46	32
0.3	15 ± 25	73 ± 21	13	64	28
0.2	9 ± 21	84 ± 21	6	86	22
0.1	15 ± 25	124 ± 21	2	111	13
0.0	-3 ± 25	152 ± 21	0	140	0

\*Calculated from:  $\Delta H^M = 124X_{Sn}^2 X_{Bi} + 140X_{Sn} X_{Bi}^2$ .

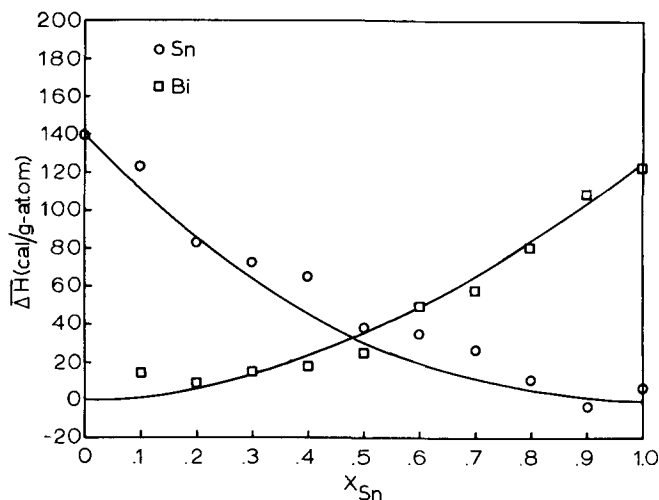


Fig. 1—Partial heats of mixing for Bi-Sn at 725 K.

number of individual measurements on which the average value is based.

### RESULTS

The experimentally determined values for the partial heats of mixing for bismuth and tin at 725 K are given in Table I along with the average bath compositions. Average values for each composition are given in Table II and plotted in Fig. 1. The curves in Fig. 1 were obtained by a regression analysis of the average values using the partial heat of mixing expressions obtained from Hardy's<sup>11</sup> subregular model in the form:

$$\overline{\Delta H}_{Sn} = 2\alpha_1 X_{Sn} X_{Bi}^2 - 2\alpha_2 X_{Sn}^2 X_{Bi} + \alpha_2 X_{Bi}^2 \quad [3]$$

and

$$\overline{\Delta H}_{Bi} = \alpha_1 X_{Sn}^2 - 2\alpha_1 X_{Sn}^2 X_{Bi} + 2\alpha_2 X_{Sn}^2 X_{Bi} \quad [4]$$

where  $\alpha_1$  and  $\alpha_2$  are constants.

The regression analysis, carried out using the 22 data points, yielded values for  $\alpha_1$  and  $\alpha_2$  of 124 and 140 respectively. Using these values and Eqs. [3] and [4] the partial heats of mixing are given by:

$$\overline{\Delta H}_{Sn} = -32X_{Sn} X_{Bi}^2 + 140X_{Bi}^2 \quad [3a]$$

and

$$\overline{\Delta H}_{Bi} = 32X_{Sn}^2 X_{Bi} + 124X_{Sn}^2 \quad [4a]$$

The integral heats of mixing have been calculated using the expression:

$$\Delta H^M = 124X_{Sn}^2 X_{Bi} + 140X_{Sn} X_{Bi}^2 \quad [5]$$

These values are given in Table II and plotted in Fig. 2 at 10 at. pct intervals.

The model proposed by Sharkey *et al.*<sup>1</sup> to describe binary heats of mixing was also used to analyze the experimental data. The integral heat of mixing, given by

$$\Delta H^M = \alpha_1 X_{Sn} X_{Bi} + \alpha_2 X_{Sn} X_{Bi}^2 - \alpha_3 X_{Sn}^2 X_{Bi}^2 \quad [6]$$

yields partial heat of mixing equations of the form:

$$\begin{aligned} \overline{\Delta H}_{Sn} &= 2\alpha_1 X_{Sn} X_{Bi}^2 + \alpha_2 (X_{Bi} - 2X_{Sn} X_{Bi}^2) \\ &\quad - \alpha_3 (2X_{Sn} X_{Bi}^2 - 3X_{Sn}^2 X_{Bi}^2) \end{aligned} \quad [7]$$

and

$$\begin{aligned} \overline{\Delta H}_{Bi} &= \alpha_1 (X_{Sn}^2 - 2X_{Sn}^2 X_{Bi}) + 2\alpha_2 X_{Sn}^2 X_{Bi} \\ &\quad - \alpha_3 (2X_{Sn}^2 X_{Bi} - 3X_{Sn}^2 X_{Bi}^2) \end{aligned} \quad [8]$$

A regression analysis of all 22 data points gave  $\alpha_1 = 126$ ,  $\alpha_2 = 142$ , and  $\alpha_3 = 15$ . These values give the following partial heat of mixing equations:

$$\overline{\Delta H}_{Sn} = -62X_{Sn} X_{Bi}^2 + 142X_{Bi}^2 + 45X_{Sn}^2 X_{Bi}^2 \quad [9]$$

and

$$\overline{\Delta H}_{Bi} = 2X_{Sn}^2 X_{Bi} + 126X_{Sn}^2 + 45X_{Sn}^2 X_{Bi}^2 \quad [10]$$

Since there is an insignificant difference between the partial and integral heats of mixing given by these two analyses, there does not appear to be any justification for the inclusion of the quasichemical correction term. The subregular model adequately describes the experimental partial heats of mixing and only values calculated using this model have been tabulated or plotted.

The results obtained in this investigation agree within experimental error with the previous results of Seltz and Dunkerley<sup>3</sup> and indicate that the integral heats of mixing, as calculated from measured partial heats of mixing, are small (<30 cal per g-atom) and endothermic.

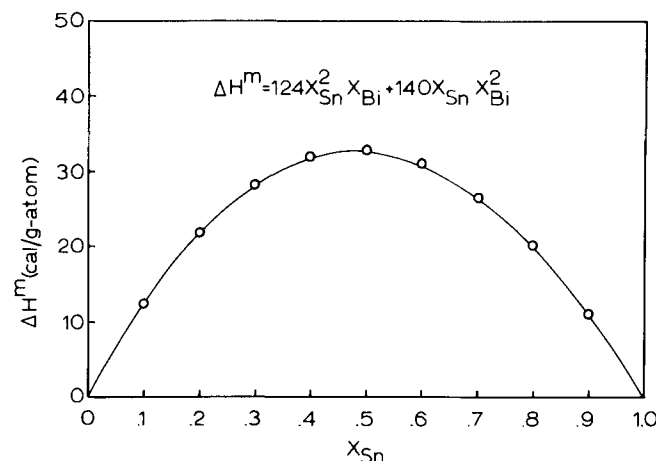


Fig. 2—Integral heat of mixing for Bi-Sn at 725 K.

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