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Behavior of the Enthalpy of Mixing in the Ternary Systems Lead-Antimony-Tin, Bismuth-Lead-Tin, and Bismuth-Cadmium-Tin at 950 K. I. Experimental Investigation

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Calorimetric studies on the enthalpies of mixing in the ternary systems Pb-Sb-Sn, Bi-Pb-Sn, and Bi-Cd-Sn have been carried out at 950 K. The partial enthalpy of mixing in the system Pb-Sb-Sn at quasi-binary section drawings goes through positive and negative regions. The partial enthalpy of mixing of lead is positive, while that of antimony is negative and takes a minimum between the quasi-binary section drawings $x_{Sn}=0$ and $x_{Sn}/x_{Pb}=6/4$. The partial molar enthalpy of mixing of bismuth in the ternary systems Bi-Cd-Sn and Bi-Pb-Sn shows level minima and the same behavior as observed for the partial enthalpy of mixing of antimony in the related system Pb-Sb-Sn. The partial enthalpy of mixing of tin in the system Bi-Pb-Sn is positive, while that of lead takes positive and negative values. Also the partial molar enthalpy of mixing of Cd in the system Bi-Cd-Sn shows a level minimum.

The binary systems of metals and metalloids have been studied in details.[1-3] In fact we have also contributed in this area.[4,5] However it appears that ternary systems have not received similar attention. Thus, the study of ternary systems from both theoretical and experimental approaches seemed of interest.

The measurements of enthalpy of mixing for binary systems and their correlation to the factors which determine the excess function behavior proved to be useful in getting insight into the behavior of such systems. It is expected that a similar approach to the ternary systems will yield better understanding of these systems. Hence we have been studying the systems Bi-Pb-Sn, Cd-Bi-Sn, and Pb-Sb-Sn in our adiabatic shield calorimeter. The experimental results of the enthalpy of mixing determinations are reported in the present paper. The analysis of the experimental results and theoretical approach to ternary solutions form the subject matter of another paper.

Experimental

Sample. The metals used were: lead of extra purity grade (E. Merck Company), 99.8 mass percent antimony (Schuchardt Company, Germany) and zone-refined 99.9999 mass percent pure tin (Koch-Light Laboratories, Ltd. England). The mixture of metals with a total mass of 149.213 g was sealed in the sample container of silica glass together with about 50 cm of 2.5 diameter silica cord. The silica cord was coiled spirally in the sample space and its purpose was to prevent breakage of the container on fusion and thermal cycling of the sample.

Calorimetric Technique. The slightly modified calorimetric apparatus was described before.[1] The calorimeter is operated with primary indirect provision of energy under adiabatic conditions. The procedures adopted were similar to those used earlier.[6,7] The 30 cm^3 sample container of silica glass has holes for heater, stirrer (made of ceramic) and a Pt-to-(Pt+10 mass per cent Rh) thermopile, axially located in the cylindrical silver calorimeter. The calorimeter-sample assembly is suspended inside a thermostat of steel (Thermax 10 FAL, production no. 4742, Germany). Below the thermostat is a heated guard system also of silver. The whole assembly is placed in a vertical tube furnace which in turn was protected by another larger one in order to obtain a double thermostat principle.

The temperature differences between the calorimeter and thermostat were measured by means of a set of fifteen differential Pt-PtRh thermopiles. These were serial connected and calibrated on a standard Pt-PtRh thermopile. The accuracy of the temperature values obtained was found to be ±0.1 K. The temperature of the guard body is kept automatically 0.2 K below that of the shield, while the temperature of the furnace is kept 5 K lower to secure satisfactory operation of the control units.

Heat capacity measurements of the empty calorimeter and thermostat were carried out in a seperate series of experiments. The C_p of the calorimeter was found to be 300 $J\,K^{-1}$ and that of the thermostat 5 $kJ\,K^{-1}$. The calibration of the calorimeter occured on exactly measured enthalpy of a standard sample of tin.[1] The time needed to reach equilibrium was registered to 430 s. The short-term fluctuation of the null point was measured to 0.3×10^{-3} $K\,min^{-1}$. The "interchange of heat constant" of the calorimeter at 973 K was estimated to 0.55 $W\,K^{-1}$. The sensibility of the calorimeter was measured to 630 $\mu V\,K^{-1}$. The thermometer resistence was measured with a Mueller bridge (Leeds & Northrup Model 8072), automated locally with stepping motors and a gated null detector, operated by a computer (Hewlett-Packard 2114B). The derived temperatures are judged to correspond with the IPTS-68 to within 0.01 K at 500 K and 0.1 K at 1000 K. In fact, the temperature increments were precisely measured to 0.0003 K.

The computer-operated energy imputs from a constant-current supply (John Fluke Current Calibrator Model 382 A) were measured with an integrating voltmeter (Hewlett-Packard Model 2401 C).

Results and Discussion

The data have been treated with the computer program Algol which searches for a set of parameters that minimizes the error square sum $h^m=(h^m_{calc}-h^m_{exp})^2$. The selected measurements comprise 36 data points corresponding the schema:

$$x_1=0, 1\,j; x_2=1\,k; x_3=0\,1\,l;$$

$$j, k, l=1\cdots\cdots 8; j+k+l=10.$$

These were symmetrical distributed in the Gibbs Triangle (x_1, x_2, and x_3 are the mole fractions of component 1, 2, and 3, respectively).

In order to save computer time, the measurement points and the values belonging to them are expressed as adjustable polynomial functions:

$$Y^e=Y^e(x_i, x_j)=\sum_{k,l} a_{kl}\, x_i^k\, x_j^l=\sum_{i,j} b_{ij}\, x_3^i\, x_1^j, \tag{1}$$

where i, j=1, 2 or 2, 3 or 3, 1. In this case, the following condition must be satisfied:

$$a_{00}=\sum_k a_{k0}=\sum_i a_{0l}=0. \tag{2}$$

Table 1. Enthalpy of Mixing in the System Pb-Sb-Sn at 950 K in J mol^{-1}. Estimated Standard Deviations in Parenthesis

x_1	x_2	x_3	h^m	x_1	x_2	x_3	h^m	x_1	x_2	x_3	h^m
0	0	X	0	5	1	4	897(5)	0	8	2	−787(2)
1	0	9	496(1)	4	2	4	349(21)	9	0	1	539(1)
0	1	9	−483(6)	3	3	4	−134(6)	8	1	1	409(1)
2	0	8	888(3)	2	2	4	−569(17)	7	2	1	231(12)
1	1	8	−5(21)	1	5	4	−989(9)	6	3	1	103(14)
0	2	8	−883(2)	0	6	4	−1299(2)	5	4	1	−37(9)
3	0	7	1168(4)	7	0	3	1202(2)	4	5	1	−170(9)
2	1	7	421(4)	6	1	3	875(16)	3	6	1	−231(11)
1	2	7	−379(19)	5	2	3	428(5)	2	7	1	−323(6)
0	3	7	−1172(3)	4	3	3	71(24)	1	8	1	−371(3)
4	0	6	1342(2)	3	4	3	−319(1)	0	9	1	−410(0)
3	1	6	709(12)	2	5	3	−650(12)	X	0	0	0(0)
2	2	6	42(15)	1	6	3	−890(10)	9	1	1	−10(0)
1	3	6	−718(7)	0	7	3	−1092(0)	8	2	0	−40(1)
0	4	6	−1343(0)	8	0	2	937(4)	7	3	0	−49(0)
5	0	5	1403(1)	7	1	2	701(2)	6	4	0	−59(1)
4	1	5	850(3)	6	2	2	380(10)	5	5	0	−59(1)
3	2	5	239(10)	5	3	2	100(7)	4	6	0	−60(0)
2	3	5	−379(0)	4	4	2	−129(5)	3	7	0	−29(1)
1	4	5	−934(5)	3	5	2	−359(7)	2	8	0	−11(1)
0	5	5	−1379(4)	2	6	2	−521(12)	1	9	0	1(2)
6	0	4	1361(0)	1	7	2	−671(2)	0	X	0	0(0)

x_1, x_2, and x_3 indicate 10 x the mole fraction of antimony, lead, and tin, respectively. The point 631 (for example) means x_1=0.6, x_2=0.3, x_3=0.1. X means 1.0.

The calculations of the coefficients b_{ij} from those a_{kl} occur by means of Algol program.

Results of the enthalpy of mixing determinations in the ternary system Pb-Sb-Sn are presented in Table 1. A number within parenthesis is the estimated standard deviation (esd.) calculated by the program. The average error of the individual measurement was found to be 1%. In fact the accuracy of the measurement results is considerably better since the enthalpy of mixing in the region near the pair Pb-Sb is small and this yields a large percentage error. To the best of our knowledge, there does not seem to be any report on the data for the enthalpy of mixing in the ternary system Pb-Sb-Sn. However, data for the binary systems Sb-Pb, Sb-Sn, and Pb-Sn with an accuracy of 1—2% have been reported earlier.[2-3,7] These date are in reasonable agreement with those obtained (for the above given pairs) in the present study on the ternary system Pb-Sb-Sn. The molar enthalpy of mixing, h^m, and the partial one of antimony at the quasi-binary section drawings Sb-Pb and Sb-Sn in the system Pb-Sb-Sn are shown in Fig. 1. The adjustable values of the integral enthalpy of mixing at the quasi-binary section drawing Pb-Sb beginning from the apex Sn are given in Table 2.

In Tables 3—5 are collected the values of the partial enthalpy of mixing of Pb, Sb, and Sn at the section

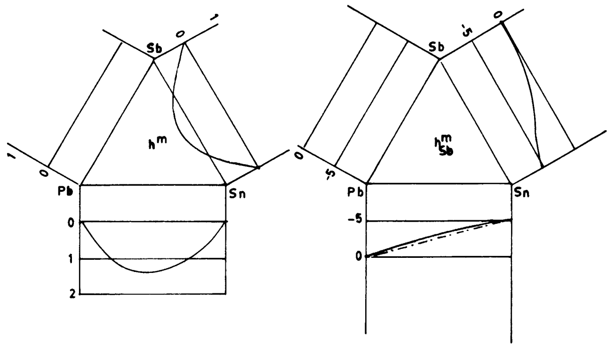

Fig. 1. The molar enthalpy of mixing, h^m, the partial one, h^m_{Sb} at the quasi-binary section drawings Sb-Pb and Sb-Sn in the system Pb-Sb-Sn at 950 K.

Table 2. Adjustable Values of the Enthalpy of Mixing (at Quasi-Binary Section Drawings Beginning from the Apex Tin) at 950 K in the System Pb-Sb-Sn in J mol^{-1}

x_{Sn}	Section drawing										
	Pb-Sn	1	2	3	4	5	6	7	8	9	Sb-Sn
0.0	0	−14	−44	−46	−51	−59	−55	−40	−13	4	0
0.1	533	437	279	141	4	−192	−193	−271	−379	−377	−422
0.2	936	749	520	282	51	−304	−304	−470	−603	−721	−801
0.3	1204	956	691	401	107	−160	−393	−599	−802	−971	−1100
0.4	1363	1107	799	491	168	−121	−399	−664	−911	−1131	−1299
0.5	1407	1139	849	538	237	−83	−381	−663	−931	−1167	−1393
0.6	1339	1097	833	547	271	−33	−319	−889	−863	−1101	−1353
0.7	1167	958	741	503	262	7	−241	−491	−714	−939	−1167
0.8	887	734	553	383	203	14	−171	−353	−526	−714	−879
0.9	486	401	301	199	99	5	−89	−201	−301	−402	−485
1.0	0	0	0	0	0	0	0	0	0	0	0

Table 3. Partial Enthalpy of Mixing of Lead (at Quasi-Binary Section Drawings Beginning from the Apex Pb) at 950 K in the System Pb-Sb-Sn in J mol^{-1}

x_{Pb}	Section drawing										
	Sn-Pb	1	2	3	4	5	6	7	8	9	Sn-Pb
0.0	317	237	561	1139	1921	2735	3564	4347	5022	5401	5165
0.1	−121	402	933	1494	2097	2714	3298	3871	4331	4632	4583
0.2	−217	361	903	1403	1891	2353	2771	3132	3451	3642	3641
0.3	−181	304	753	1182	1575	1925	2222	2563	2617	2714	2733
0.4	−132	246	612	963	1272	1534	1727	1865	1963	1984	2014
0.5	−93	186	473	756	973	1174	1296	1391	1431	1441	1438
0.6	−39	163	354	553	697	815	898	943	974	969	993
0.7	−22	121	242	334	434	501	543	554	581	573	600
0.8	5	57	121	163	201	222	241	253	247	255	265
0.9	8	21	31	40	46	52	46	49	61	54	58
1.0	0	0	0	0	0	0	0	0	0	0	0

Table 4. Partial Enthalpy of Mixing of Antimony (at Quasi-Binary Section Drawings Beginning from the Apex Sb) at 950 K in the System Pb-Sb-Sn in J mol^{-1}

x_{Sb}	Section drawing										
	Sn-Sb	1	2	3	4	5	6	7	8	9	Pb-Sb
0.0	−5501	−3891	−4431	−3991	−3571	−3163	−2702	−2151	−1455	−669	−43
0.1	−5496	−5572	−5591	−5472	−5214	−4814	−4706	−3910	−2923	−1725	−271
0.2	−5651	−5964	−6114	−6037	−5661	−5113	−4432	−3627	−2693	−1585	−321
0.3	−5713	−6042	−6144	−5598	−5646	−5113	−4437	−3640	−2691	−1585	−294
0.4	−5582	−5791	−5791	−5573	−5165	−4603	−3922	−3153	−2286	−1341	−244
0.5	−5122	−5234	−5160	−4913	−4507	−3982	−3363	−2681	−1917	−1107	−169
0.6	−4595	−4417	−4327	−4124	−3796	−3375	−2854	−2285	−1634	−900	−38
0.7	−3472	−3464	−4400	−3270	−3051	−2747	−2364	−1900	−1322	−620	250
0.8	−2550	−2490	−2423	−2330	−2193	−1990	−1700	−1284	−760	−70	814
0.9	−1863	−1641	−1450	−1246	−1037	−800	−490	−90	431	1063	1880
1.0	0	0	0	0	0	0	0	0	0	0	0

Table 5. Partial Enthalpy of Mixing of Tin (at Quasi-Binary Section Drawings Beginning from the Apex Tin) at 950 K in the System Pb-Sb-Sn in J mol^{-1}

x_{Sn}	Section drawing										
	Pb-Sn	1	2	3	4	5	6	7	8	9	Sb-Sn
0.0	5950	5084	3681	2203	990	−242	−1240	−2221	−3204	−4081	−4350
0.1	4803	3881	2753	1590	484	−518	−1432	−2248	−2299	−3633	−3998
0.2	3617	2904	2133	1304	462	−371	−1137	−1871	−2521	−3091	−3540
0.3	2647	2181	1668	1130	524	−86	−714	−1318	−1901	−2432	−2913
0.4	1922	1614	1302	950	555	107	−360	−830	−1293	−1738	−2197
0.5	1363	1151	952	730	481	194	−131	−454	−794	−1142	−1504
0.6	902	751	602	482	317	163	−33	−231	−441	−665	−894
0.7	511	397	325	244	163	83	−21	−120	−230	−343	−480
0.8	215	162	119	83	50	11	−33	−70	−114	−155	−199
0.9	44	33	20	8	−5	−9	−20	−31	−40	42	−60
1.0	0	0	0	0	0	0	0	0	0	0	0

drawings Sb-Sn, Sn-Pb, and Pb-Sb beginning with the apices Pb, Sb, and Sn, respectively. From these data one may observe that $h_{\mathrm{Sb}}^{\mathrm{m}}$ takes only negative values, $h_{\mathrm{Pb}}^{\mathrm{m}}$ is positive while $h_{\mathrm{Sn}}^{\mathrm{m}}$ goes through positive and negative regions. Figure 2 shows the partial enthalpy of mixing of antimony at the quasi-binary section drawing Sn-Pb beginning from the apex Sb in the system Pb-Sb-Sn. It is clearly observable that $h_{\mathrm{Sb}}^{\mathrm{m}}$ takes a minimum between the quasi-binary section drawings $x_{\mathrm{Sn}}=0$ and $x_{\mathrm{Sn}}/x_{\mathrm{Sb}}=6/4$.

It is expected that the partial molar enthalpy of mixing of bismuth in the ternary systems Bi-Cd-Sn and Bi-Pb-Sn shows the same behavior as observed for $h_{\mathrm{Sb}}^{\mathrm{m}}$ in the related system Pb-Sb-Sn. In order to decide this, we have also been studying these two systems. In Tables 6 and 7 are presented the values of $h_{\mathrm{Bi}}^{\mathrm{m}}$ at quasi-binary section drawings in the systems Bi-Pb-Sn and Bi-Cd-Sn beginning from the apex Bi. Figure 3 shows the integral enthalpy of mixing, h^{m}, at the quasi-binary section drawings in the system Bi-Pb-Sn. $h_{\mathrm{Si}}^{\mathrm{m}}$ is also shown in this figure. The integral enthalpy of mixing takes positive values in the pairs Pb-Sn and

Sn-Bi, while h^m is negative in the pair Bi-Pb. This was also recognized by Wittig in his study on these binary systems.[1,2] A somewhat surprising observation is that h^m_{Bi} in Bi-Pb-Sn indicates a level minimum in the region between the quasi-binary section drawings $x_{Sn}=0$ and $x_{Pb}/x_{Sn}=6/4$. As indicated in Fig.4, h^m_{Sn} takes positive values while h^m_{Pb} goes through positive and negative regions.

Figure 5 shows the integral enthalpy of mixing, h^m, and the partial molar one of Bi, h^m_{Bi}, at the quasi-binary

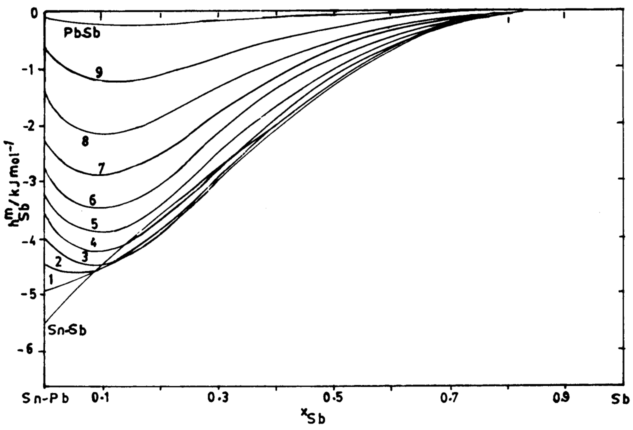

Fig. 2. Partial enthalpy of mixing of antimony at the quasi-binary section drawing Sn-Pb beginning from the apex Sb in the system Pb-Sb-Sn at 950 K.

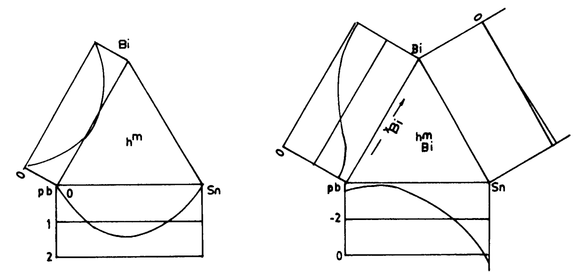

Fig. 3. Partial enthalpy of mixing of bismuth at quasi-binary section drawings in the system Bi-Pb-Sn and the integral enthalpy of mixing at 950 K.

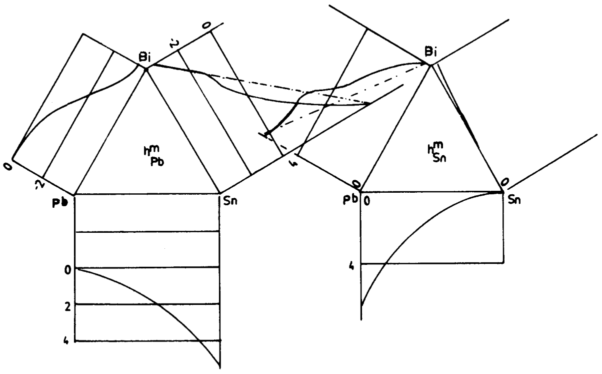

Fig. 4. Partial enthalpy of mixing of Pb and Sn at quasi-binary section drawings in the system Bi-Pb-Sn at 950 K.

Table 6. Partial Molar Enthalpy of Mixing of Bismuth (at Quasi-Binary Section Drawings Beginning from the Apex Bi) at 950 K in the System Bi-Pb-Sn in J mol^{-1}

x_{Bi}	Section drawing										
	Bi-Pb	1	2	3	4	5	6	7	8	9	Bi-Sn
0.0	−3705	−3298	−2976	−2679	−2397	−2121	−1820	−1450	−979	−344	392
0.1	−3572	−3166	−3041	−2976	−2836	−2624	−2334	−1950	−1447	−826	351
0.2	−3006	−2566	−2630	−2399	−2482	−2285	−2016	−1388	−1252	−675	301
0.3	−2510	−1990	−2023	−1978	−1861	−1685	−1460	−884	−882	−418	149
0.4	−2015	−1410	−1400	−1348	−1228	−1110	−946	−590	−552	−239	96
0.5	−1009	−842	−829	−824	−756	−667	−515	−373	−321	−189	75
0.6	−852	−460	−356	−282	−202	−178	−166	−154	−142	−131	71
0.7	−753	−202	−157	−125	−91	−82	−71	−64	−55	−43	58
0.8	−251	−156	−125	−101	−75	−64	−60	−51	−48	−39	48
0.9	−75	−72	−72	−62	−58	−54	−51	−42	−38	−34	41
1.0	0	0	0	0	0	0	0	0	0	0	0

Table 7. Partial Molar Enthalpy of Mixing of Bismuth (at Quasi-Binary Section Drawings Beginning from the Apex Bi) at 950 K in the System Bi-Cd-Sn in J mol^{-1}

x_{Bi}	Section drawing										
	Cd-Bi	1	2	3	4	5	6	7	8	9	Sn-Bi
0.0	9420	8398	7580	6825	6108	5407	4642	3699	2500	1135	381
0.1	7620	8063	7746	7582	7228	6690	5955	4976	3696	2112	364
0.2	6190	6537	6700	6113	6327	5828	5145	4227	3198	1727	392
0.3	4905	5070	5155	5041	4744	4298	3727	3046	2253	1325	294
0.4	3440	3570	3570	3436	3130	2833	2415	1940	1412	822	146
0.5	1988	2240	2207	2100	1927	1702	1438	1143	823	470	73
0.6	1207	1213	1187	1129	1040	924	784	764	547	245	69
0.7	536	535	524	502	469	411	364	345	298	94	57
0.8	415	413	418	405	387	372	352	337	216	88	56
0.9	381	381	379	376	365	351	339	316	199	78	32
1.0	0	0	0	0	0	0	0	0	0	0	0

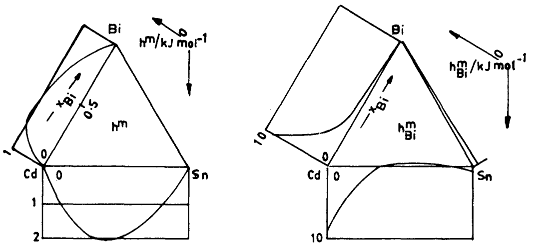

Fig. 5. Integral enthalpy of mixing and partial enthalpy of mixing of bismuth at quasi-binary section drawings in the system Bi-Cd-Sn at 950 K.

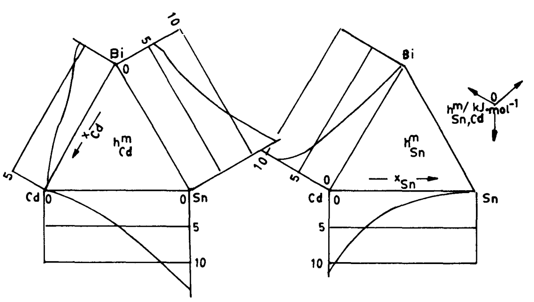

Fig. 6. Partial enthalpy of mixing of Cd and Sn at quasi-binary section drawings in the system Bi-Cd-Sn at 950 K.

section drawings Bi-Cd and Bi-Sn in the system Bi-Cd-Sn. It is clearly observable that h^m takes a maximum at $x_{Cd}=x_{Sn}=0.5$. h^m is also positive in the pairs Bi-Cd and Sn-Bi. As we have expected, h^m_{Sb} takes also a striking level minimum in the region $x_{Sn}=0$ to $x_{Cd}/x_{Sn}=6/4$. This means that there exists a general property for ternary systems.

Figure 6 shows the partial molar enthalpy of mixing of Cd and Sn at the quasi-binary section drawings Bi-Cd and Bi-Sn. h^m_{Cd} exhibits also a level minimum. However, the level minimum of Cd and the bend joined to this minimum disappear rapidly when the mole fraction of Sn increases. At the same time the bend of h^m_{Bi} in the pairs Bi-Cd and Bi-Sn shows always positive trends.

On the basis of our discussion, we come to the following conclusion: There exists a general property which predicts the behavior of mixing in ternary systems. This property could be overlapped by other ones belonging to the pairs of components in the ternary systems. In fact, this property is recognized in the present study and will be reported together with the theoretical analysis of the experimental results in the second part of this work.

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