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Thermodynamic Properties of Liquid Zinc—Bismuth Alloys

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With 5 Figures

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Thermodynamic properties of liquid Zn—Bi alloys were investigated between 5 and 95 at% Zn from the liquidus curve to 750 °C using an *emf* method with a molten salt electrolyte. Partial and integral values were calculated and compared with results from the literature. From the *emf* data the liquidus curve was calculated. The thermodynamic data of the Zn—Bi system are well established and consistent with the phase diagram. The entropies of mixing of various group IIB—VA systems are compared and discussed with respect to compound formation in the liquid state.

In a series of investigations we have studied the thermodynamic properties of liquid group IIB—VA alloy systems[1–5]. By quasi-continuous *emf* measurements a significant temperature dependence of thermodynamic properties was found in several systems[1, 4, 5] which had escaped detection by the more conventional *emf* measurements of previous investigators. It was therefore decided, in spite of numerous *emf* studies[6–13], to reinvestigate the thermodynamic properties of liquid zinc—bismuth alloys by carefully and quasi-continuously recording the *emf* as a function of temperature.

The zinc—bismuth phase diagram as compiled by *Hansen* and *Anderko*[14] shows a miscibility gap between 37 and 99.4 at% Zn with a critical point at ≈ 605 °C and ≈ 84 at% Zn, a monotectic temperature at 416 °C and a eutectic point at 254.5 °C and 8.1 at% Zn. The liquidus of the miscibility gap is mainly based on the *emf* measurements of *Kleppa*[6], and it has been confirmed by similar work of *Martin-Garin* et al.[13].

Thermodynamic activities of zinc—bismuth alloys have been measured by the following investigators with the concentration ranges given in parentheses: *Kleppa*[6] ($N_{\mathrm{Zn}} = 0.06$—0.97), *Kleppa* and

Thalmayer[7] ($N_{Zn} = 0.70$—0.95), *Lantratov* and *Tsarenko*[8] ($N_{Zn} = 0.14$—0.97), *Gluck* and *Pehlke*[9] ($N_{Zn} = 0.02$—0.05), *Chiba*, *Matsushima* and *Ono*[10] ($N_{Zn} = 0.07$—0.39), *Ptak* and *Moser*[11] ($N_{Zn} = 0.05$—0.90), *Moser*[12] ($N_{Zn} = 0.01$—0.07), *Martin-Garin*, *Bedon* and *Desré*[13] ($N_{Zn} = 0.02$—0.95). Calorimetric determinations of enthalpies of mixing have been reported by *Kawakami*[15] ($N_{Zn} = 0.17$—0.81), by *Wittig*, *Müller* and *Schilling*[16] ($N_{Zn} = 0.10$—0.95), and by *Gambino*[17] ($N_{Zn} = 0.06$—0.94). A consistent set of thermodynamic data of liquid zinc—bismuth alloys has been compiled by *Hultgren* et al.[18] based on published data[6, 7, 10–12, 16]. In the present investigation the *emf* between liquid zinc—bismuth alloys of various compositions and pure liquid zinc with a liquid KCl—LiCl—$ZnCl_2$ electrolyte was measured quasi-continuously as a function of temperature from about 750 °C down to the liquidus curve.

Experimental Procedure

The metals, 4 N zinc and 5 N bismuth, were purchased from ASARCO (New Jersey, USA), the salts, KCl, LiCl and $ZnCl_2$, were p. A. products of E. Merck (Darmstadt).

The metals were further purified by melting under vacuum and filtering through quartz wool. The metals were weighed on an analytical balance (± 0.05 mg), and the alloys were prepared in the *emf* cell. The electrolyte, a eutectic mixture of KCl and LiCl with 0.4 mole% $ZnCl_2$, was purified at 720 K by passing Cl_2 for approximately one hour through the melt, followed by Ti-gettered argon. The *emf* cell and the four capillaries, with Mo-wire sealed into them, were made of quartz. The cell had a thermocouple well in the center and was sealed on top with a brass head. The cell arrangement was $Zn(l)/Zn^{2+}(KCl—LiCl)(l)/Zn(N_{Zn})Bi(1—N_{Zn})(l)$. The temperature was measured with a chromel-alumel thermocouple calibrated at the melting points of 5 N Cd, Zn and Sb. The cell was heated in a metal block furnace made of antimagnetic stainless steel which was heated by three separate electric circuits. The uniformity of temperature within the cell was better than 0.1 K. The *emf* was continuously measured with a voltmeter (2402 A Integrating Digital Voltmeter, Hewlett Packard, USA) combined with a small computer (Hewlett Packard, USA). The cell was operated at a reduced pressure of Ti-gettered argon (600 torr at 700 K). The four electrodes were inserted into the molten electrolyte and the cell was held at 900 K for several hours until the *emf* became stable. It was then heated up to 1,000 K at the rate of 6 K per hour and cooled at the same rate. Readings were taken every 1 K, and at approximately every 50 K the cell was held at constant temperature and the *emf* measured as a function of time. These isothermal measurements agreed with those determined on heating and on cooling within the limits of error. During each run three heating and three cooling curves were taken. The maximum deviation between a heating and a subsequent cooling curve was 50 to 100 μV.

The composition of the alloys after completion of an experiment was checked by chemical analysis. The alloys were dissolved in dilute HNO_3, the pH adjusted to 2, and the bismuth content determined by titration

Table 1. *Experimental Results of emf Measurements on Liquid* Zn—Bi *Alloys*

Composition at% Zn	$E = a + b\,T$ (K)		a_{Zn} (923 K)	$\Delta \overline{H}_{\mathrm{Zn}}$ (cal · g-atom^{-1})	$\overline{S}^{xs}_{\mathrm{Zn}}$ (e.u.)	c_1	c_2	Liquidus temperature (°C)
	a	$b \cdot 10^3$						
95.05	— 2.160	3.443	0.9747	99.6	0.058	0.0252	0.0543	547
89.88	— 5.560	7.378	0.9691	256.4	0.128	0.0752	0.1398	586
84.86	— 7.468	9.674	0.9639	344.4	0.120	0.1274	0.1875	605
75.17	— 12.895	15.908	0.9560	594.6	0.167	0.2359	0.3241	594
65.23	— 21.089	26.267	0.9236	972.4	0.362	0.3478	0.5301	550
59.70	— 24.506	31.232	0.8969	1130.0	0.415	0.4075	0.6160	530
56.93	— 28.000	36.071	0.8753	1291.1	0.544	0.4301	0.7038	520
52.10	— 31.976	42.109	0.8408	1474.5	0.646	0.4786	0.8038	497
50.25	— 32.821	43.115	0.8390	1513.4	0.621	0.5172	0.8250	488
40.45	— 41.506	58.754	0.7261	1913.9	0.911	0.5850	1.0433	434
32.20	— 47.577	72.341	0.6171	2193.9	1.084	0.6501	1.1960	399 *
16.70	— 59.228	104.837	0.3891	2731.1	1.280	0.8445	1.4888	335 *

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* Computed from Eq. 4.

with a $0.1N$-*EDTA* solution using xylenole orange as indicator. The pH was then changed to 10 and the zinc content also found by titration with a $0.1N$-*EDTA* solution with buffer tablets (E. Merck, Darmstadt) as indicator. Since the change in the composition of the alloys was within the limits of error of the chemical analysis, the nominal composition was taken as actual composition with the error $\delta N_{\mathrm{Zn}} < 0.002$. The errors of the temperature measurements are δT (abs.)/K = 0.5 and δT (diff.)/K = 0.2.

Experimental Results and Discussion

Emf measurements were carried out on alloys of the following compositions (in at% Zn): 16.72, 32.21, 40.45, 50.25, 52.10, 56.93, 59.67, 65.23, 75.17, 84.86, 89.88, and 95.05. For all alloys the *emf* data showed very little scatter (10 to 15 μV) and varied linearly with temperature within the precision of the measurements and the temperature range studied. The experimental points, about 100 per 100 K for each experimental composition in the temperature range between liquidus temperature and 1,000 K, could therefore be expressed in terms of two coefficients, a and b, which are listed in Table 1.

Consequently simple relationships exist between the *emf* E and the partial excess thermodynamic functions shown by the following equations.

$$\mu^{xs}_{\mathrm{Zn}}/RT = -n\,FE/RT - \ln N_{\mathrm{Zn}} = c_1 + c_2\,(T_0/T - 1) \quad (1)$$

$$\Delta\,\overline{H}_{\mathrm{Zn}}/RT = c_2 T_0/T \quad (2)$$

$$\overline{S}^{xs}_{\mathrm{Zn}}/R = -\,(c_1 - c_2) \quad (3)$$

The coefficients c_1 and c_2 are also listed in Table 1. At the reference temperature $T_0 = 923.2$ K we get $\mu^{xs}_{\mathrm{Zn}}(T_0)/RT_0 = c_1$, and $\Delta\,\overline{H}_{\mathrm{Zn}}/RT_0 = c_2$. Activities (at 923 K) and partial molar properties of zinc referred to liquid zinc as the standard state are given in Table 1. The partial molar excess entropy of zinc is shown in Fig. 1, and the partial molar enthalpy of zinc in Fig. 2. In both figures the results of other authors who have studied a major part of the concentration range are plotted for comparison. The agreement between the various sets of data is generally very good. Only the results of *Chiba* et al.[10] and of *Lantratov* and *Tsarenko*[8] deviate significantly from the rest. The solid lines drawn through our data points for $\overline{S}^{xs}_{\mathrm{Zn}}$ and $\Delta\,\overline{H}_{\mathrm{Zn}}$ both show a small bump near the critical concentration. The effect, however, is very small, and any correlation with the critical point is rather tentative.

Since the *emf* vs. T-curves show a distinct break at the liquidus temperature, information about the phase diagram can be obtained from *emf* measurements. The liquidus temperatures thus obtained are given in Table 1 and plotted in Fig. 3. The phase boundary of the miscibility gap was also calculated at various temperatures by finding the points of contact of the common tangents to ΔG^M-composition curves. These data too are shown in Fig. 3. Points on the liquidus in equilibrium with solid zinc were obtained from the thermodynamic data of the liquid alloys (Table 1) and of pure zinc by graphically solving the equation for the equilibrium transfer of one gramatom of zinc from the solid state (s) into the liquid solutions (ls):

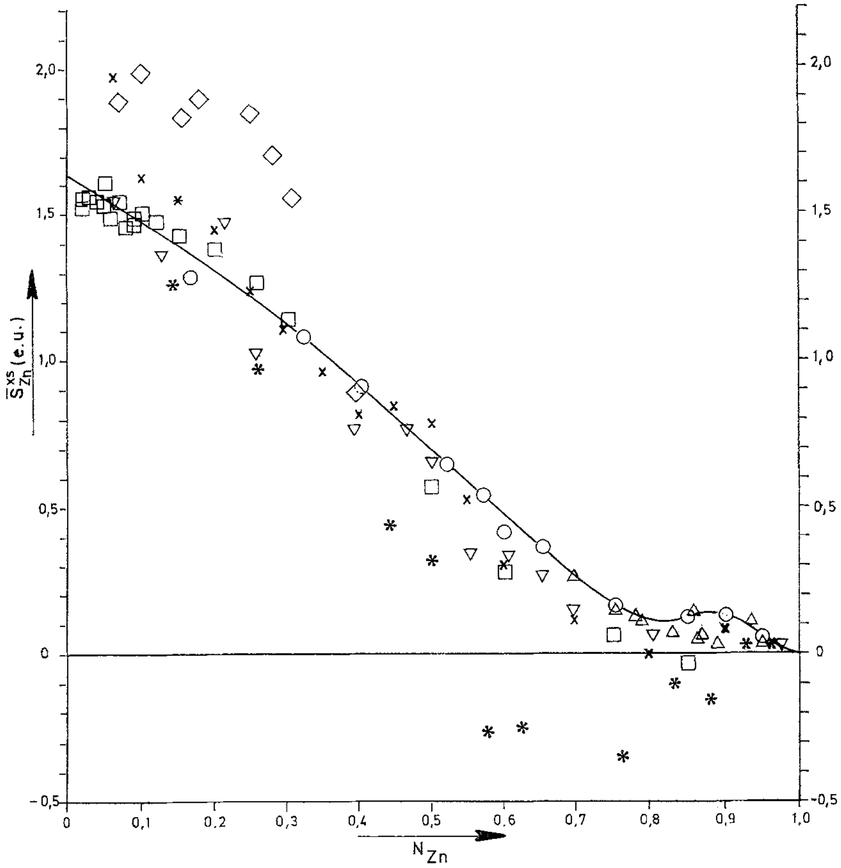

Fig. 1. Partial excess entropy of zinc of liquid zinc—bismuth alloys: ✱ *M. F. Lantratov* and *E. V. Tsarenko*[8]; ◇ *Y. Chiba* et al.[10]; △ *O. J. Kleppa* and *C. E. Thalmayer*[7]; □ *L. Martin-Garin* et al.[13]; ▽ *O. J. Kleppa*[7]; × *W. Ptak* and *Z. Moser*[11]; ○ present investigation

$$\mathrm{Zn}\,(s) = \mathrm{Zn}\,(ls)\quad \Delta G = 0 = \Delta G_F + \Delta \bar{G}^{ls}_{\mathrm{Zn}} = \Delta G_F + RT \ln a^{ls}_{\mathrm{Zn}} \quad (4)$$

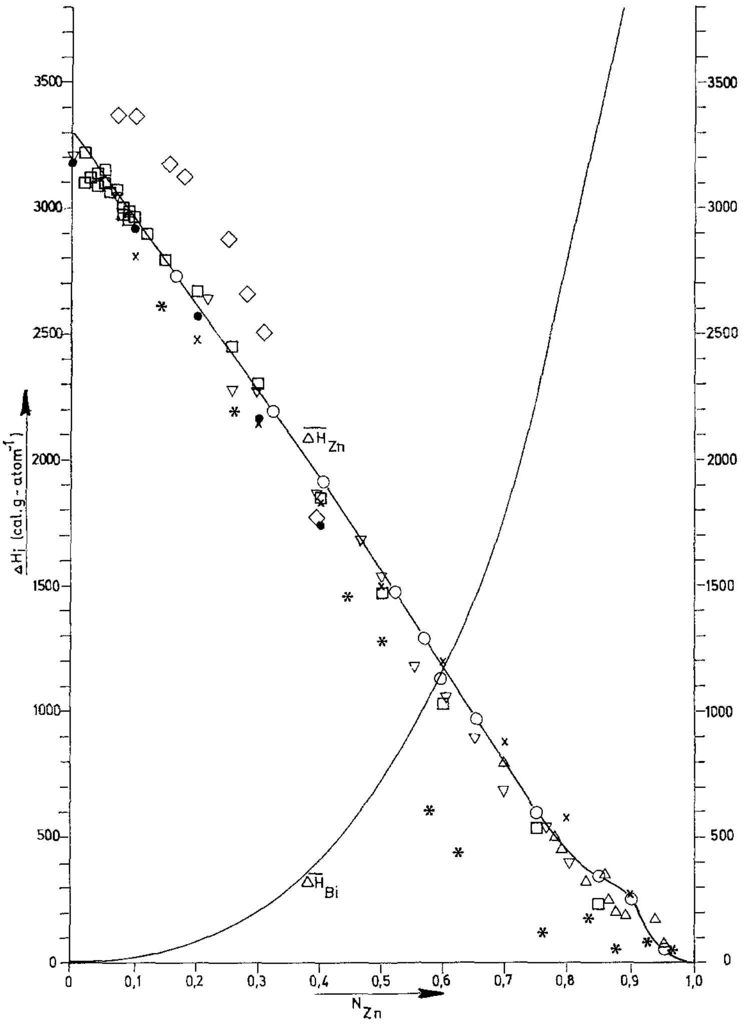

Fig. 2. Partial enthalpy of zinc of liquid zinc—bismuth alloys: ● *F. E. Wittig* et al.[16]; other symbols see Fig. 1

The free energy of fusion of zinc was calculated from the data given by *Kubaschewski*, *Evans*, and *Alcock*[19]. The results are included in Table 1 and Fig. 3. The data points fall with some scatter on a smooth curve indicating that the phase diagram and the thermodynamic data are consistent. The critical point was found to be at 84 at% Zn and 605 °C. The good agreement between our data and the results of *Kleppa*[6] and *Martin-Garin* et al.[13] in Fig. 3 is added support for the liquidus curve

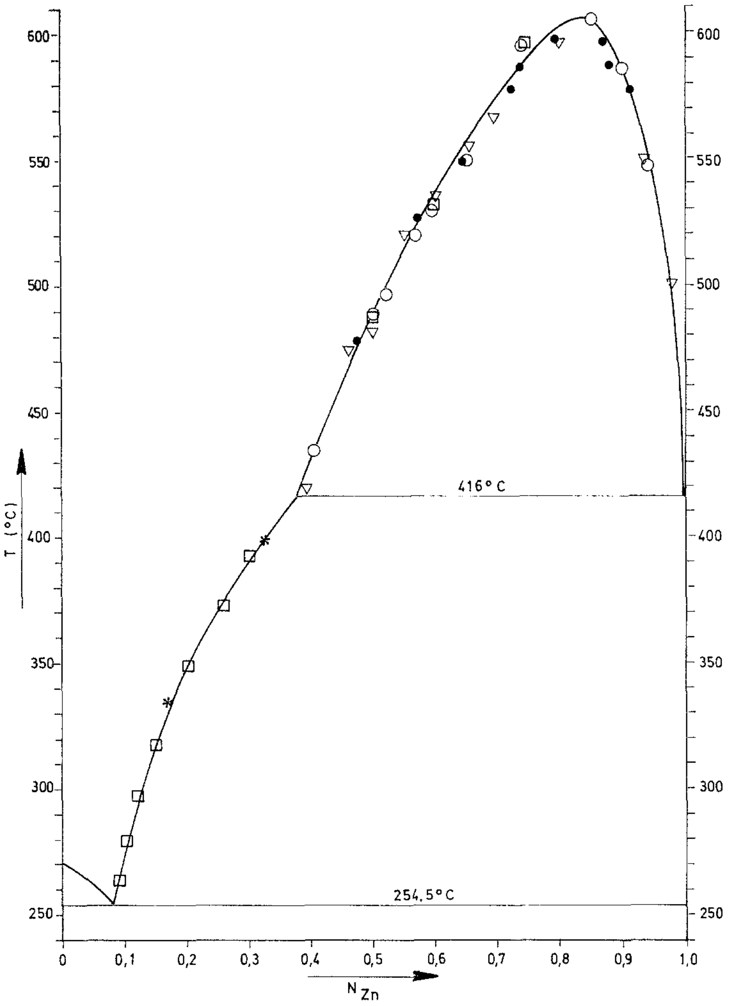

Fig. 3. Zinc—bismuth phase diagram: □ *L. Martin-Garin* et al.[13]; ▽ *O. J. Kleppa*[6]; ○ ● ✳ present investigation (○ from breaks in *emf* vs. *T* curves; ● computed from ΔG^M vs. N_{Zn} curves; ✳ computed from Eq. 4)

selected by *Hansen*[14]. No explanation can be given for the extreme asymmetry of the miscibility gap reported by *Ptak* and *Moser*[11].

Partial molar functions of bismuth and integral molar quantities were calculated by *Gibbs-Duhem* integrations of $\Delta \bar{H}_{Zn}$ and $\alpha_{Zn} = \ln \gamma_{Zn}/(1\text{-}N_{Zn})^2$. The data, referred to liquid zinc and liquid bismuth as standard states, are listed in Table 2. The integral molar enthalpy of mixing is

Table 2. *Thermodynamic Properties of Liquid Zinc—Bismuth Alloys at 923 K*

N_{Zn}	$-\Delta G^M$ (cal · g-atom^{-1})	ΔH^M (cal · g-atom^{-1})	ΔS^M (e.u.)	a_{Bi}	$\Delta \overline{H}_{Bi}$ (cal · g-atom^{-1})	$\overline{S}^{xs}_{Bi}$ (e.u.)
0.1	416.3	306.5	0.783	0.907	16.6	0.086
0.2	584.5	578.4	1.260	0.823	83.0	0.046
0.3	662.2	802.5	1.587	0.750	201.5	0.103
0.4	676.3	978.0	1.792	0.670	382.0	0.207
0.5	639.0	1091.5	1.875	0.604	683.0	0.373
0.6	564.5	1134.8	1.841	0.540	1147.5	0.665
0.7	459.7	1088.3	1.677	0.498	1737.8	0.960
0.8	334.0	928.4	1.367	0.470	2770.1	1.295
0.9	197.9	632.9	0.900	0.452	4070.4	1.435

shown in Fig. 4, and the integral molar entropy of mixing in Fig. 5. With the exception of the results by *Lantratov* and *Tsarenko*[8] the enthalpy of mixing data derived from *emf* measurements are in good agreement. Surprisingly the calorimetric values of *Wittig* et al.[16] are somewhat less positive then the other data. The slight increase of ΔH^M with increasing temperature between 450° and 600 °C on the Bi-rich side

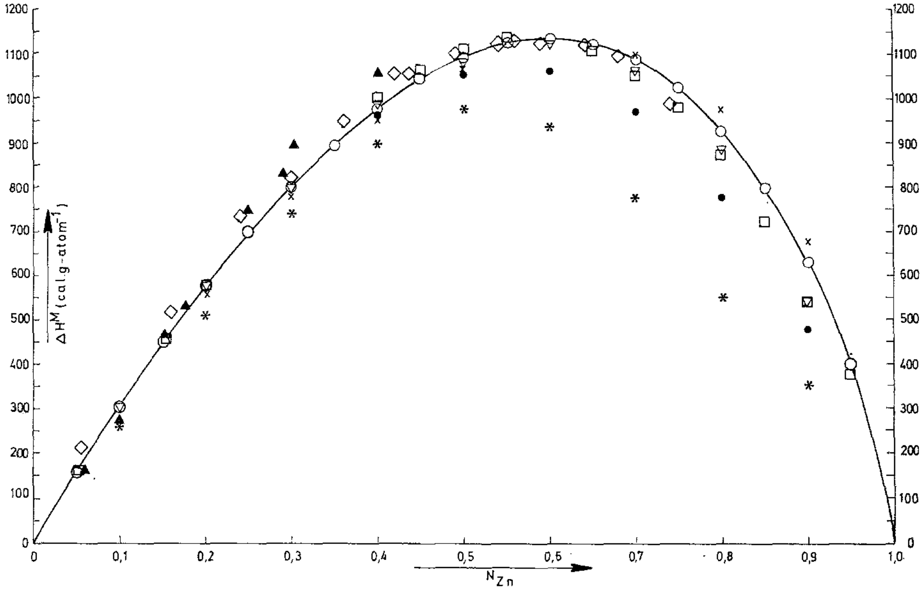

Fig. 4. Enthalpy of mixing of liquid zinc—bismuth alloys: ✱ *M. F. Lantratov* and *E. V. Tsarenko*[8]; □ *L. Martin-Garin* et al.[13]; ● *F. E. Wittig* et al.[16]; ◇ *M. Gambino* (873 K)[17]; ▽ *O. J. Kleppa*[6]; × *W. Ptak* and *Z. Moser*[11]; ▲ *Y. Chiba* et al.[10]; ○ present investigation

as observed by *Gambino*[17] could not be verified since our *emf* vs. T curves were linear. Only C_p measurements on liquid alloys could tell whether the effect is real or whether it might have been caused by slow equilibration close to the miscibility gap. In Fig. 5 the entropies of mixing close to the liquidus temperature of liquid alloys of the various group IIB—VA systems[1, 2, 4, 5] are compared. In systems with compound formation in the liquid state[1, 4, 5] the ΔS^M-parabolas show a significant depression which is explained by the existence of compound clusters of the stoichiometry $(\mathrm{IIB})_4(\mathrm{VA})_3$ in the melt. The curves for Cd—Bi and Zn—Bi alloys are parabolas showing no signs of compound formation in the liquid state. In all five systems the ΔS^M-parabolas are more positive than the curve for the ideal entropy of mixing.

Bedon and *Desré*[20] have measured the density of Bi-rich liquid Zn—Bi alloys and found at 460 °C an inflection in the isothermal density vs. composition curve close to the eutectic composition. The excess volume of mixing of liquid Zn—Bi alloys at 460 °C was found to be negative for compositions between 0 and 6 at% Zn and positive for all other compositions[21]. Although no correlation could be established between the excess volume of mixing and the excess entropy of mixing, it was intimated that the inflection in the partial excess entropy of Zn and the negative values of the partial excess volume of Zn for Bi-rich alloys could point to an ordering effect in these alloys[13]. Defining an "average chemical local order effect" in liquid alloys *Bellissent-Funel* and *Desré*[22] could show that in liquid Zn—Bi alloys the maximum of the "average chemical local order" occurs close to the eutectic composition.

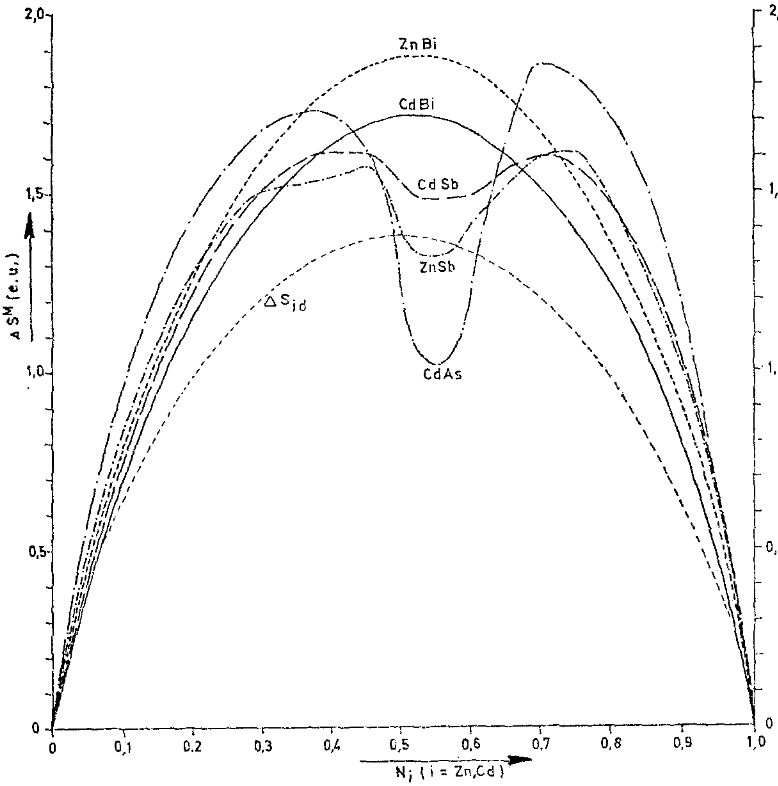

Fig. 5. Entropy of mixing of liquid alloys in the systems Cd—Sb[1], Cd—Bi[2], Zn—Sb[4], Cd—As[5], and Zn—Bi (present investigation)

The partial and integral thermodynamic properties of lqiuid Zn—Bi alloys did not exhibit any of the anomalies previously observed in Cd—Sb[1, 3], Zn—Sb[4], and Cd—As[5] alloys at 57 at% Cd and Zn, resp., which have been associated with compound formation in the melts. As was the case with liquid Cd—Bi alloys[2] replacement of As or Sb by Bi greatly diminishes the tendency for compound formation in the alloys. The ordering effect observed by *Desré* and coworkers[13, 20–22] in Zn—Bi alloys occurs at the eutectic composition (8.1 at% Zn). It is due to attractive interaction between like atoms and is not caused by compound formation. The small anomalies in the $\Delta \overline{H}_{\mathrm{Zn}}$- and $\overline{S}^{xs}_{\mathrm{Zn}}$-curves (Figs. 1 and 2) on the Zn-rich side are also thought to be due to attractive interaction between like atoms.

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