Bull. Chem. Soc. Jpn., 63, 1795—1780 (1990)

The Behavior of Mixing in Liquid Binary Alloys. Enthalpies of Mixing in the Systems Lead-Tin, Lead-Antimony, Lead-Bismuth, and Lead-Thallium

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(Received December 2, 1988)

The paper presents values of the enthalpy of mixing in the liquid systems Sn-Sb, Pb-Bi, and Tl-Pb. The enthalpy of mixing in the system Sn-Sb is positive with a maximum of about 1.4 kJ mol^{-1}. The enthalpies of mixing in the systems Pb-Sb, Pb-Bi, and Tl-Pb are slight negative (−0.07 to −1) kJ ml^{-1}. The enthalpy of mixing and the ξ-function in the above given systems rule for liquid systems of B-metals.

In our previous study[1] on the system tin-antimony, it was observed that the enthalpy of mixing, $\Delta_m H^\circ$ and the ξ-function which is given by

$$\xi = \frac{\Delta_m H^\circ}{x_2(1-x_2)} \tag{1}$$

where x_2 is the mole fraction of the second component, exhibit minima around 40 at% Sb. Furthermore, it was observed that the absolute value of the limiting partial molar enthalpy of mixing of antimony is higher than that of tin in accordance with the rules by Wittig and Gehring[2] where the partial molar enthalpy of mixing of the metal with higher valency is larger than that of the metal with the lower valency. This observation was in contrast to that found by some earlier groups.[3–5] The present study decides whether the enthalpy of mixing and the ξ-function as predicted before[1] may rule for liquid systems of B-metals or not.

The enthalpy of mixing depends on the ratio of the atomic radii and the electronegativity of the components. With reference to these factors, the present study on the above given systems shows that the enthalpy of mixing depends upon the position of the components in the periodic table and suggests rules for such a dependence.

Another point of interest is to see how the enthalpy of mixing correlate with the volume of mixing using the data obtained from our study[6] on the same systems given above. These systems have been selected due to their freedom from miscibility gaps. Furthermore, the study on systems from homologous series in the periodic table proved to be useful in understanding the behavior of thermodynamic properties of metallic alloys.

Experimental

Sample. The metals used were of extra purity grade (E. Merck Co.). The preparation, treatment and testing of the samples were all the same as described before.[7] The procedure adopted in the present study was similar to that used earlier.[8] In the measurement process, the samples of different masses (1.467—1.679 g) were dropped in a liquid phase of the same composition and material as that of the solid sample.

Calorimetric Technique. The calorimetric apparatus and measurement technique have been described in detail in the previous paper[8] along with results for measurement on the enthalpy of a standard sample of tin. The hollow space of the cylindrical calorimeter of Thermax steel which serves as a sample container is coated with a layer of aluminum oxide. The role of the Al_2O_3 layer is to prevent reaction of the sample with the metallic calorimeter. The calorimeter has wells for the drop device, ceramic stirrer and thermocouple. The calorimeter is suspended inside a metallic shield system of refined steel. This contains two cylindrical compensating systems of Thermax steel placed below and above the calorimeter. The lower compensating system has wells of each 3.5 mm diameter for twelve differential Pt-to-(Pt+10 mass percent Rh) thermocouples. The whole assembly is placed in a vertical tube furnace. A second tube furnace is placed above the cooling system which in turn was placed at the upper part of a silica glass tube containing the whole assembly. The role of the second tube furnace was to temper the sample before its final drop in the calorimeter.

The calibration of the thermocouples used is based on a standard Pt-PtRh thermocouple. 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.

The calibration of the calorimeter is conducted by measuring the enthalpy difference of a standard sample of tin.[9]

Results and Discussion

(i) Enthalpies. Values of the enthalpy differences of the metals Pb, Sn, Sb, Bi, and Tl are presented in Tables 1—5. The average error of the individual

Table 1. Experimentally Determined Enthalpy Difference of Lead in kJ mol^{-1}. M(Pb)=207 g mol^{-1}

T/K[a)]	$H^\circ(T)-H^\circ$(298.15 K)	T/K	$H^\circ(T)-H^\circ$(298.15 K)
298.15	0	700.09	17.289
400.02	2.798	800.01	20.149
499.98	5.729	899.98	22.965
600.45(s)	8.897	1000.03	25.748
600.45(l)	14.370	1099.98	28.549

a) The approximate temperature increments can be inferred from the adjacent mean temperature.

Table 2. Experimentally Determined Enthalpy Difference of Tin in kJ mol^{-1}. M(Sn)=118.69 g mol^{-1}

T/K	$H^\circ(T)-H^\circ(298.15\text{ K})$	T/K	$H^\circ(T)-H^\circ(298.15\text{ K})$
298.15	0	800.01	21.466
400.01	2.851	900.03	24.309
505.06(s)	5.822	999.98	27.155
505.06(l)	13.021	1100.02	32.739
599.98	15.685	1200.00	32.851
700.02	18.622	—	—

Table 3. Experimentally Determined Enthalpy Difference of Antimony in kJ mol^{-1}. M(Sb)=121.75 g mol^{-1}

T/K	$H^\circ(T)-H^\circ(298.15\text{ K})$	T/K	$H^\circ(T)-H^\circ(298.15\text{ K})$
298.15	0	800.01	13.550
400.05	2.627	900.04	16.551
500.01	5.340	904.43(s)	16.673
600.03	7.921	904.43(l)	36.549
699.98	10.688	1000.01	39.566

Table 4. Experimentally Determined Enthalpy Difference of Bismuth in kJ mol^{-1}. M(Bi)=208.98 g mol^{-1}

T/K	$H^\circ(T)-H^\circ(298.15\text{ K})$	T/K	$H^\circ(T)-H^\circ(298.15\text{ K})$
298.15	0	544.56(l)	17.907
400.06	2.708	601.01	19.550
499.98	5.488	699.98	22.475
544.56(s)	6.771	800.03	25.331

Table 5. Experimentally Determined Enthalpy Difference of Thallium in kJ mol^{-1}. M(Tl)=204.37 g mol^{-1}

T/K	$H^\circ(T)-H^\circ(298.15\text{ K})$	T/K	$H^\circ(T)-H^\circ(298.15\text{ K})$
298.15	0	600.03	13.214
400.01	2.789	698.87	16.297
500.07	5.822	800.05	19.532

measurement was found to be about 0.34% while the deviation for a single measurement of earlier reported data10) is about 1%.

(ii) Enthalpies of Mixing. Equations which could be used for determining of the enthalpy of mixing have been given earlier.7) Table 6 presents values of the integral and partial molar enthalpy of mixing for the system Sn-Pb at 1040 K in the whole range of composition. A number within parenthesis is the estimated standard deviation (e.s.d.). The accuracy obtained is 0.5%. The present value is in good agreement with that found previously.10,11) The following polynomial functions are derived using curve-fitting calculations to produce the curves for $\Delta_m H^\circ$, $\Delta_m H^\circ_{Sn}$, and $\Delta_m H^\circ_{Pb}$ as shown in Fig. 1 (x_2: the mole fraction of Pb):

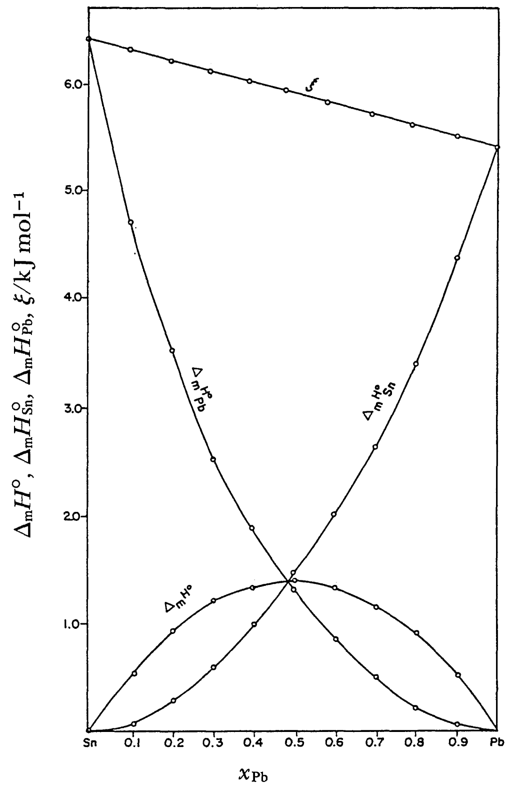

Fig. 1. Integral and partial molar enthalpy of mixing for the liquid system Sn-Pb at 1040 K.

Table 6. Integral and Partial Molar Enthalpies of Mixing: Values for the Liquid System Sn-Pb at 1040 K in kJ mol^{-1}; Estimated Standard Deviations in Parenthesis

x_{Pb}	$\Delta_m H^\circ$		$\Delta_m H^\circ_{Sn}$	$\Delta_m H^\circ_{Pb}$	ξ
	Present study	Hutgren et al.10)			
0	0	0	0	6.400	6.400(00)
0.1	0.550(15)	0.544	0.084	4.742	6.273(20)
0.2	0.941(14)	—	0.297	3.517	6.145(20)
0.3	1.201(15)	1.192	0.603	2.595	6.018(18)
0.4	1.344(13)	—	0.986	1.880	5.890(19)
0.5	1.382(15)	1.368	1.450	1.313	5.763(20)
0.6	1.317(17)	—	2.006	0.858	5.941(17)
0.7	1.152(14)	1.146	2.672	0.500	5.508(20)
0.8	0.882(14)	—	3.465	0.236	5.380(19)
0.9	0.505(13)	0.502	4.172	0.073	5.253(20)
1.0	0[a]	—	5.448	0[a]	5.125(320)

a) Extrapolated value.

Table 7. Integral and Partial Molar Enthalpies of Mixing: Values for the Liquid System Pb-Sb in kJ mol^{-1}; Estimated Standard Deviations in Parenthesis

x_{Sb}	$\Delta_m H^\circ$ Present study	$\Delta_m H^\circ$ Hutgren et al.[10]	$\Delta_m H^\circ_{Pb}$	$\Delta_m H^\circ_{Sb}$	ξ
0	0	0	0	0.097	+0.097(0)
0.1	0.000(5)	0	0.009	−0.078	−0.110(2)
0.2	−0.015(5)	—	0.025	−0.174	−0.122(3)
0.3	−0.037(6)	−0.034	0.031	−0.196	−0.176(3)
0.4	−0.058(7)	—	0.012	−0.163	−0.246(2)
0.5	−0.070(5)	−0.067	0.039	−0.100	−0.280(3)
0.6	−0.069(7)	—	−0.119	−0.036	−0.279(3)
0.7	−0.054(6)	−0.050	−0.199	0.008	−0.258(3)
0.8	−0.030(5)	—	−0.231	0.020	−0.205(3)
0.9	−0.009(6)	−0.008	−0.130	0.004	−0.103(2)
1.0	0[a]	—	0.224	0[a]	+0.011(2)

a) Extrapolated value.

$$\Delta_m H^\circ = 6.400\ x_2 - 9.647\ x_2^2 + 6.869\ x_2^3 - 4.880\ x_2^4 + 1.275\ x_2^5, \tag{2}$$

$$\Delta_m H^\circ_{Sn} = 9.647\ x_2^2 - 13.739\ x_2^3 + 14.641\ x_2^4 - 5.101\ x_2^5, \tag{3}$$

$$\Delta_m H^\circ_{Pb} = 6.400 - 19.295\ x_2 + 30.256\ x_2^2 - 33.261\ x_2^3 + 21.019\ x_2^4 - 5.101\ x_2^5. \tag{4}$$

The integral enthalpy of mixing in the system Sn-Pb is positive and increases with the increase of lead mole fraction to reach a maximum at 50 at-% Pb; after that, the enthalpy of mixing decreases with increasing lead mole fraction.

The partial molar enthalpy of mixing of tin is positive but decreases with the increase of lead mole fraction.

The partial molar enthalpy of mixing of lead is also positive and increases with increasing composition of Pb. This behavior is understandable: the insertion of the larger lead atom in the structure is associated with a positive deformation work which increases with increasing composition since the structure exhibits higher tension. At higher composition, the structure becomes instable.

According to the definition of the ξ-function (Eq. 1), we obtain through Eq. 2 the following linear polynomial function for ξ:

$$\xi(T) = 6.400 - 1.275\ x_2. \tag{5}$$

The values of ξ are listed in Table 6. Figure 1 shows the linear trend of the ξ-function.

In Table 7 are collected the values of the integral and partial molar enthalpies of mixing for the liquid system Pb-Sb together with those for the ξ-function at 907 K as determined in the present study. The present value ford $\Delta_m H^\circ$ is in excellent agreement with that obtained by Hultgren et al.[10] (see Table 7). From curve fitting calculations, the following polynomial function for $\Delta_m H^\circ$ is derived (x_2: the mole fraction of Sb):

$$\Delta_m H^\circ = 0.097\ x_2 - 1.059\ x_2^2 + 0.764\ x_2^3 + 1.439\ x_2^4 - 1.253\ x_2^5. \tag{6}$$

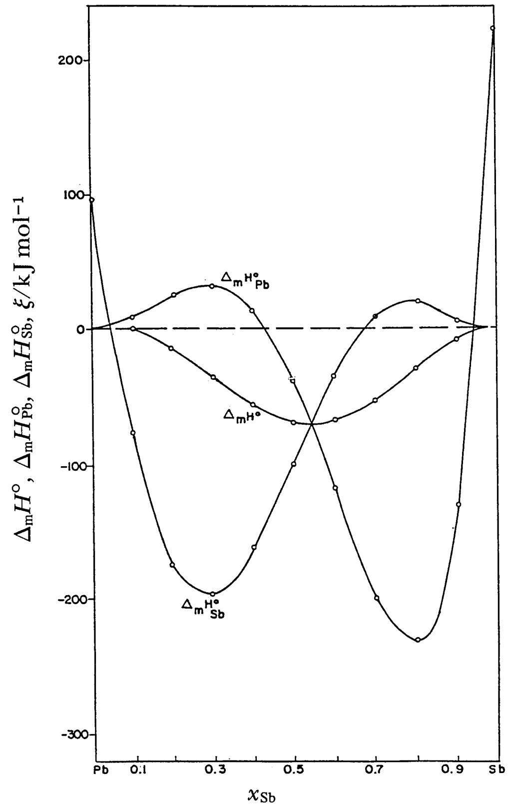

Fig. 2. Integral and partial molar enthalpy of mixing for the liquid system Pb-Sb at 907 K.

Figure 2 shows the curves $\Delta_m H^\circ$, $\Delta_m H^\circ_{Pb}$, and $\Delta_m H^\circ_{Sb}$ against the mole fraction of antimony, x_{Sb}. The integral enthalpy of mixing is slightly negative and takes a minimum at x_{Sb}=0.55. Also the partial molar enthalpies of mixing of Pb and Sb go through this minimum. The present study on the system Pb-Sb also provides the conclusions: both enthalpy and volume of mixing are slight negative, correlation between the behavior of the enthalpy of mixing and that of the volume of mixing.

With reference to the definition of the partial molar quantities (see Ref.7), we obtain through Eq. 6 the following polynomial function for $\Delta_{\rm m}H^{\circ}_{\rm Pb}$ and $\Delta_{\rm m}H^{\circ}_{\rm Sb}$ (x_2: the mole fraction of Sb):

$$\Delta_{\rm m}H^{\circ}_{\rm Pb}=1.059x_2^2-1.529\,x_2^3-4.318\,x_2^4+5.012\,x_2^5, \quad (7)$$

$$\Delta_{\rm m}H^{\circ}_{\rm Sb}=0.097-2.119\,x_2+3.353\,x_2^2-4.229\,x_2^3-10.583\,x_2^4+5.012\,x_2^5. \quad (8)$$

Figure 2 shows the curves of the partial molar enthalpies of mixing of lead and antimony against the mole fraction of antimony, $x_{\rm Sb}$.

The partial molar enthalpy of mixing of lead, $\Delta_{\rm m}H^{\circ}_{\rm Pb}$ goes through negative region lying between x_2=0.05 and x_2=0.675 with a minimum at the composition 30 at % Sb. Around the composition 70 at % Sb, $\Delta_{\rm m}H^{\circ}_{\rm Pb}$ becomes slightly positive with a maximum at 80 at % Sb. This also indicates the maximum of $\Delta_{\rm m}H^{\circ}_{\rm Sb}$ which takes positive values in the region lying between x_2=0 and x_2=0.4.

The partial molar enthalpy of mixing of Sb is negative in the region lying between x_2=0.4 and x_2=0.95. This indicates the stability of the structure which decreases with increasing composition of Sb. Above the composition 95 at % Sb, $\Delta_{\rm m}H^{\circ}_{\rm Sb}$ increases rapidly since the structure starts to collapse.

Table 7 illustrates values for the ξ-function in the system Pb-Sb. The results have been least squares fitted by a polynomial expression. The trend of ξ deviates from linearity if $\Delta_{\rm m}H^{\circ}$ far from the parabolic form as a function of x_2. The ξ-function is negative with a minimum at x_2=0.5. This indicates the stability of the structure in the entire range of composition. However, the stability decreases with the increase of Sb mole fraction.

In Table 8 are collected the values of the integral and partial molar enthalpies of mixing for the liquid system Pb-Bi together with those for the ξ-function at 700 K as determined in the present study. These are in acceptable agreement with those obtained by Hultgren et al.[10] (see Table 8). Based upon curve-fitting calculations, the following polynomial function for $\Delta_{\rm m}H^{\circ}$is derived (x_2: the mole fraction of Bi):

$$\Delta_{\rm m}H^{\circ}=-4.483\,x_2+5.557\,x_2^2-1.074\,x_2^3. \quad (9)$$

Figure 3 shows the curve of the enthalpy of mixing against the temperature. The enthalpy of mixing is negative in the whole range of composition and takes a minimum at x_2=0.5.

Using Eq. 9 and the definition of the partial molar quantities (Ref. 7), the following polynomial functions for $\Delta_{\rm m}H^{\circ}_{\rm Pb}$ and $\Delta_{\rm m}H^{\circ}_{\rm Bi}$ are derived:

$$\Delta_{\rm m}H^{\circ}_{\rm Pb}=-5.557\,x_2^2+2.148\,x_2^3, \quad (10)$$

$$\Delta_{\rm m}H^{\circ}_{\rm Bi}=-4.483+11.114\,x_2-8.779\,x_2^2+3.138\,x_2^3. \quad (11)$$

Figure 3 shows the plot of $\Delta_{\rm m}H^{\circ}_{\rm Pb}$ and $\Delta_{\rm m}H^{\circ}_{\rm Bi}$ versus the mole fraction of Bi, x_2.

The partial molar enthalpy of mixing of lead is negative and becomes more negative at higher composition of Bi.

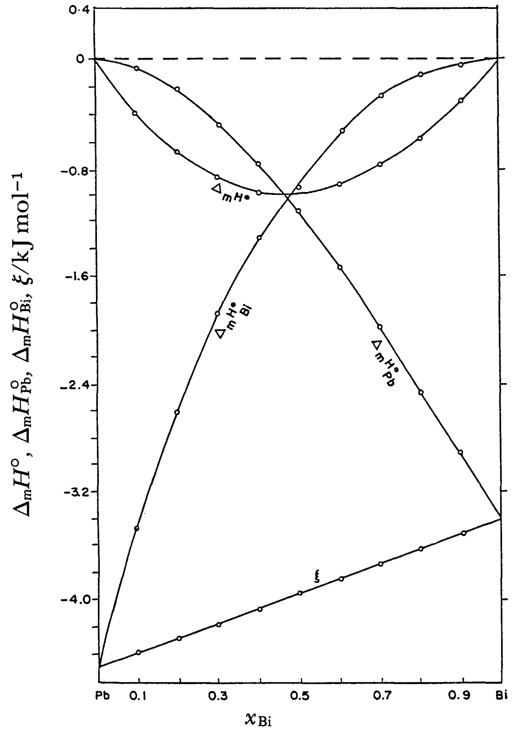

Fig. 3. Integral and partial molar enthalpy of mixing for the liquid system Pb-Bi at 700 K.

Table 8. Integral and Partial Molar Enthalpies of Mixing: Values at 700 K for the Liquid System Pb-Bi in kJ mol^{-1}; Estimated Standard Deviations in Parenthesis

$x_{\rm Bi}$	$\Delta_{\rm m}H^{\circ}$		$\Delta_{\rm m}H^{\circ}_{\rm Pb}$	$\Delta_{\rm m}H^{\circ}_{\rm Bi}$	ξ
	Present study	Hutgren et al.[10]			
0	0	0	0	−4.483	−4.483(0)
0.1	−0.394(4)	−0.335	−0.053	−3.457	−4.376(3)
0.2	−0.682(7)	—	−0.205	−2.594	−4.268(5)
0.3	−0.874(7)	−0.879	−0.442	−1.881	−4.161(4)
0.4	−0.973(9)	—	−0.752	−1.305	−4.053(7)
0.5	−0.987(8)	−0.108	−1.121	−0.852	−3.946(7)
0.6	−0.921(9)	—	−1.537	−0.511	−3.839(4)
0.7	−0.784(7)	−0.900	−1.986	−0.268	−3.731(6)
0.8	−0.580(6)	—	−2.457	−0.111	−3.624(3)
0.9	−0.319(5)	−0.335	−2.935	−0.025	−3.516(5)
1.0	0	—	−3.409	0	−3.409(0)

Table 9. Integral and Partial Molar Enthalpies of Mixing: Values at 775 K for the Liquid System Tl-Pb in kJ mol^{-1}; Estimated Standard Deviations in Parenthesis

x_{Pb}	$\Delta_m H^\circ$		$\Delta_m H^\circ_{Tl}$	$\Delta_m H^\circ_{Pb}$	ξ
	Present study	Hutgren et al.[10)]			
0	0	0	0	−3.498	−3.498(0)
0.1	−0.330(7)	−0.326	−0.021	−3.112	−3.468(7)
0.2	−0.615(6)	—	−0.098	−2.683	−3.437(7)
0.3	−0.842(6)	−0.837	−0.263	−2.194	−3.407(7)
0.4	−0.996(5)	—	−0.549	−1.666	−3.377(9)
0.5	−1.061(7)	−1.054	−0.976	−1.146	−3.347(3)
0.6	−1.027(5)	—	−1.539	−0.686	−3.316(5)
0.7	−0.891(5)	−0.883	−2.189	−0.335	−3.286(5)
0.8	−0.661(5)	—	−2.820	−0.122	−3.256(7)
0.9	−0.362(6)	−0.368	−3.259	−0.040	−3.226(6)
1.0	0[a)]	—	−3.243	0[a)]	−3.195(47)

a) Extrapolated value.

The partial molar enthalpy of mixing of bismuth is also negaitve but increases with the increase of bismuth mole fraction. This behavior is understandable: the insertion of the larger bismuth atom in the structure causes a positive deformation work. At higher composition, the structure exhibits higher tension so that the structure becomes instable.

Values of the ξ-function for the liquid system Pb-Bi are given in Table 8. The following linear polynomial function is derived with the aid of Eq. 9 to produce the linear relation of ξ to the mole fraction of Bi as shown in Fig. 3;

$$\xi(T) = -4.493 + 1.181\, x_2. \qquad (12)$$

It is apparent that ξ (700 K) exhibits a negative increasing trend that indicates the stability of the structure which becomes less stable at higher composition of Bi.

Table 9 presents values of the integral and partial molar enthalpies of mixing and the ξ-function at 775 K for the liquid system Tl-Pb. A number within parenthesis is the estimated standard deviation (e.s.d.). The accuracy obtained in the present study for enthalpy of mixing measurement is 0.5%. The present value is in excellent agreement with that obtained by Hultgren et al.[10)] (see Table 9). From curve-fitting calculations, the following polynomial function for $\Delta_m H^\circ$ is derived (x_2: the mole fraction of Pb):

$$\Delta_m H^\circ = -3.498\, x_2 + 1.914\, x_2^2 + 0.292\, x_2^3 + 4.283\, x_2^4 - 3.026\, x_2^5. \qquad (13)$$

Figure 4 shows the curve of $\Delta_m H^\circ$ against the mole fraction of lead, x_2.

The integral enthalpy of mixing for the liquid system Tl-Pb is negative in the whole range of composition.......with a maximum lying at 50 at% Pb.

With reference to the definition of the partial molar quantities, we obtain with the aid of Eq. 13 the following polynomial functions for $\Delta_m H^\circ_{Tl}$ and $\Delta_m H^\circ_{Pb}$:

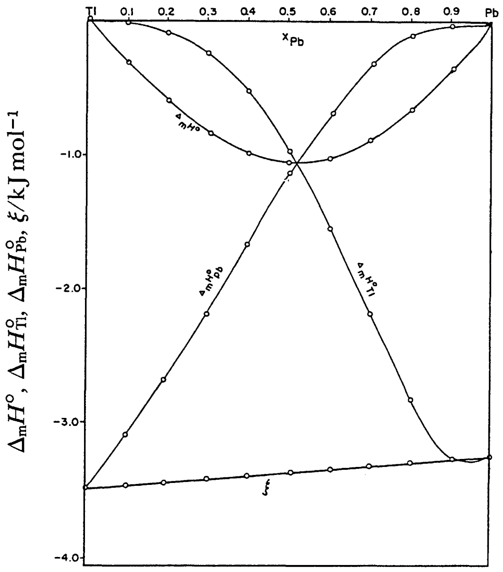

Fig. 4. Integral and partial molar enthalpy of mixing in the liquid system Tl-Pb at 775 K.

$$\Delta_m H^\circ_{Tl} = -1.914\, x_2^2 - 0.583\, x_2^3 - 12.850\, x_2^4 + 12.105\, x_2^5, \qquad (14)$$

$$\Delta_m H^\circ_{Pb} = -3.498 + 3.828\, x_2 - 1.039\, x_2^2 + 16.550\, x_2^3 - 27.981\, x_2^4 + 12.105\, x_2^5. \qquad (15)$$

The partial molar enthalpy of mixing of thallium is negative and becomes more negative at higher composition. The behavior of the enthalpy of mixing in the system Tl-Pb is similar to that of $\Delta_m H^\circ$ in the related system Pb-Bi. The explanation for the behavior of $\Delta_m H^\circ_{Pb}$ in the system Tl-Bi is the same as that for $\Delta_m H^\circ_{Bi}$ in the system Pb-Bi: the insertion of the larger Pb atom in the structure leads to a positive deformation work. Due to higher tensions, the structure becomes instable at higher composition.

Table 9 also illustrates values for the ξ-function in the liquid system Tl-Pb. These were obtained from calculations according to the following linear polynomial function:

$$\xi(T) = -3.498 + 0.303\, x_2. \tag{16}$$

The ξ-function is negative in the whole range of composition but increases at higher composition of Pb. This indicates the structure stability which decreases at higher composition of Pb. Such a behavior has also been observed for the ξ-function in the liquid system Pb–Bi.

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