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Behaviors of the Enthalpies of Mixing and Formation in the System Lead-Indium

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The paper presents results of calorimetric studies on the enthalpies of mixing and formation in the system lead–indium. The enthalpy of formation is negative and becomes more negative at higher composition. The partial enthalpy of formation of lead is negative but increases at higher composition. The partial enthalpy of formation of indium is also negative and decreases with increasing the composition. The enthalpy of formation displays a considerable temperature dependence which seems to be smaller than that observed for the enthalpy of formation in other systems.

The studies of the behavior of the enthalpy of formation, $\Delta_f H^\circ$, in binary systems begun in the previous papers[1,2] are now continued with another system, namely lead–indium. The phase diagram of this system has been previously studied by Hansen[3] and Elliott.[4] Also the enthalpy of solution has been measured by Hultgren et al.[5] However, no determination of the enthalpy of formation in the system Pb–In seems to be reported so far. Hence we report here values for the enthalpy of formation at 298.15 K and 423 K.

The studies by Wittig and Schöffl[6] on the enthalpy of formation in the systems Al–Ag and Al–Zn revealed a pronounced temperature dependence of $\Delta_f H^\circ$. Such a temperature dependence was claimed to be a general property of all metallic alloys. On the other hand, the increase of the heat of formation due to an increase in the temperature was attributed to lattice defects of greater expansion of aluminum lattice in the alloys compared with the expansion in pure aluminum metal. However, such a lattice defect caused by the increase in the temperature is not common to all metallic solid solutions. Thus, further studies on other systems are required in order to decide if a pronounced temperature dependence of $\Delta_f H^\circ$ is general property of all metallic alloys. For this reason, we have been studying the system Pb–In which was selected due to its large range of miscibility in the solid state.

Experimental

Sample. The metals used were of extra purity grade (Riedel de Haen Co.). The preparation, treatment, and testing of the samples were all the same as described before.[1] The samples were tempered for 6 h at 420 K, 6 h at 350 K, and 190 h at 320 K. The procedure adopted was similar to that used earlier.[2] In the measurement process, the samples of different masses (1.352—1.525 g) were dropped in a liquid phase (having the same composition and material as that of the solid sample) existing inside the calorimeter.

Apparatus. The calorimeter operates quasi-isothermally and represents an isoperibolic calorimeter. Figure 1 shows the apparatus which consists of a cooling system (10) in which a tube of silica glass (20), of 85 mm diameter and 800 mm height, with lower closed end was fixed by means of sealing-wax. The tube of silica glass contains a cylindrical shield system of V2A steel (13) being connected to a ring of brass by means of three rods of V2A steel. The ring of brass is placed in the lower part of the cooling system.

A set of plates of Nickel (12) are connected to the cover of the shield by means of three rods of V2A steel and their purpose was to distribute the heat radiation.

The cylindrical shield (ϕ_e=80 mm, ϕ=68 mm, h=200 mm) contains two cylindrical compensating systems of Thermax steel (14, 18) placed below and above a calorimeter also of Thermax steel (Thermax 10, production no. 4742, Germany). The hollow space of the calorimeter (16) is coated with a layer of aluminum oxide in order to provide better

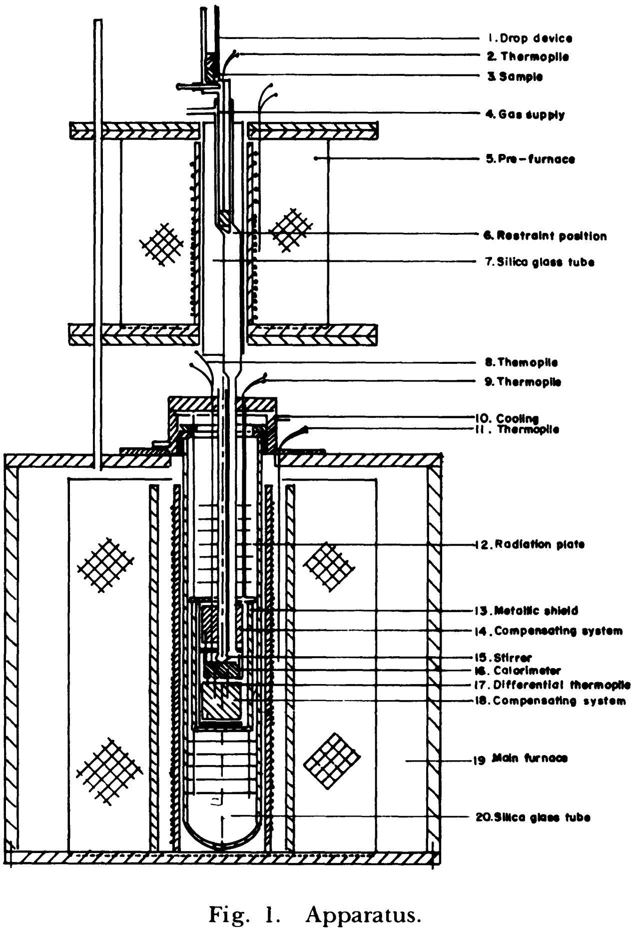

Fig. 1. Apparatus.

interchange of heat and to prevent reaction with the sample since the calorimeter was used as a sample container. The lower compensating system (18) was connected to a plate of V2A steel by means of two rods of the same material. This plate was used as a cover of the shield.

The change of the calorimeter after completion of a series of experiments occurs by moving the upper compensating system upwards.

The lower compensating system is connected to the calorimeter by means of a set of twelve differential Pt-to-(Pt+10 mass per cent Rh) thermopiles. These were calibrated on a standard Pt–PtRh thermopile. The cover of the calorimeter (sprayed with Al_2O_3) has three wells for the thermopile of the calorimeter (8), stirrer made of ceramic (15) and the silica glass tube of the drop device.

The upper compensating system (14) having the same dimensions as those of the lower one is placed on three studs made of ceramic. The differential thermopiles (17) and other ones have leeds which go through wells in the cover of the cooling system. These are sealed by means of lip sealing in form of rubber rings.

The whole assembly is placed in a vertical tube furnace (19) of 41 Ω resistance. Another vertical tube furnace (5) of 35 Ω resistance is placed above the cooling system. The role of the second furnace was to warm the sample before its final drop in the calorimeter. The drop of the sample to a position lying close to the center of the upper tube furnace occurs by means of a drop device (1). The restrain development (6) allows the sample to be tempered at any temperature. The final drop of the samle occurs by moving the upper part of the drop device upwards. The drop device is connected with argon gas supply (4) being connected with a purification and distribution device. The role of Ar gas is to prevent oxidation.

The temperature differences between the calorimeter and the lower compensating system were measured by means of a set of twelve differentical Pt–PtRh thermopiles. The sensibility of the thermopiles was increased due to isolation of their soldered joints with a layer of aluminum oxide instead of tubes of ceramic. This also reduced the dead time of the calorimeter. Excellent regulation of the temperature of the furnace was obtained by means of p-regulator.[7] The temperature of the guard body is kept 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. The calibration of the calorimeter was conducted measuring the enthalpy of a standard sample of tin.[8] The calibration factor was determined with an accuracy of 0.3%. The time needed to reach equilibrium was registered to 300 s. The calorimeter sensibility is 625 μV K^{-1}. The short-term fluctuation of the null point was measured to 2.1×10^{-2} K min^{-1}. The temperature drifts of the calorimeter from the lower compensating system were of negligible importance. 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 precision is considerably better and, the temperature increments were measured to 0.0003 K. The measurement of the thermal potential of the thermopiles occured by means of a digital millivoltmeter (Hewlett-Packard 2401 C).

Results and Discussion

(i) Enthalpies. Table 1 presents values of $H_1^\circ(T)-H_1^\circ(298.15\ \mathrm{K})$; $H_1^\circ(T)-H_1^\circ(423\ \mathrm{K})$ and $H_2^\circ(T)-H_2^\circ(298.15\ \mathrm{K})$; $H_2^\circ(T)-H_2^\circ(423\ \mathrm{K})$ as determined in the present study. The average error of the individual measurements was found to be 0.34% while the deviation for a single measurement of earlier reported data[5] was estimated to 1%.

Table 2 summarizes values of $[H_3^\circ(670\ \mathrm{K})-H_3^\circ(298.15\ \mathrm{K})]$ and $[H_3^\circ(720\ \mathrm{K})-H_3^\circ(423\ \mathrm{K})]$. The deviation is 0.32% for a single measurement.

(ii) Enthalpy of Mixing. The enthalpy of mixing of lead–indium at the temperature T_1 has been determined according to the following equations:

$$-(1-x_2)\cdot \mathrm{Pb}(l, T_1) - x_2 \cdot \mathrm{In}(l, T_1) + \mathrm{Pb}_{1-x_2}\mathrm{In}_{x_2}(l, T_1) = 0 \tag{1}$$

$$\Delta_m H^\circ = -(1-x_2)H_1^\circ(T_1) - x_2 H_2^\circ(T_1) + H_3^\circ(T_1) \tag{2}$$

where $\Delta_m H^\circ$ is the enthalpy of mixing of liquid Pb–In and H_3° is the enthalpy of the alloy at the mole fraction of indium x_2.

Table 1. Experimentally Determined Enthalpy Differences of Lead and Indium. M(Pb)=207.2 g mol^{-1}; M(In)=114.82 g mol^{-1}

T/K[a]	$H_1^\circ(T)-H_1^\circ(298.15\ \mathrm{K})$	$H_1^\circ(T)-H_1^\circ(423\ \mathrm{K})$	$H_2^\circ(T)-H_2^\circ(298.15\ \mathrm{K})$	$H_2^\circ(T)-H_2^\circ(423\ \mathrm{K})$
	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
298.15	0	—	0	—
400.01	2.796	—	2.509	—
429.45(s)	—	—	3.509	—
429.45(l)	—	—	7.168	3.460
499.98	5.726	2.189	9.243	5.547
600.45(s)	8.891	6.275	12.162	8.496
600.45(l)	14.361	10.545	—	—
670.03	16.407	12.617	14.188	10.521
700.11	17.280	13.503	15.053	11.391
719.97	17.860	14.089	15.627	11.970
800.13	20.151	16.412	17.916	14.272
900.02	22.960	19.259	20.075	17.125

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

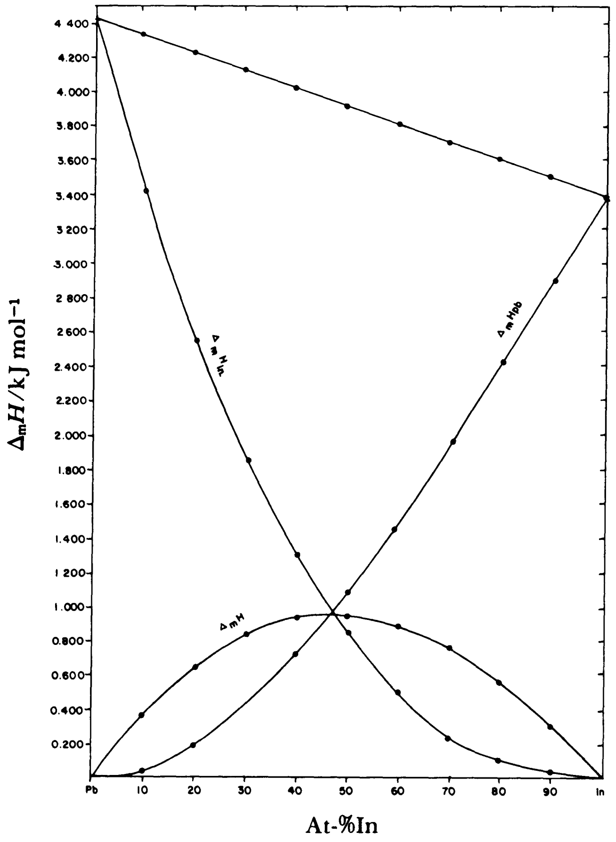

Fig. 2. The integral and partial molar enthalpies of mixing; the ξ-function at 670 K in the system Pb–In.

Table 3 collects the values of the integral and partial molar enthalpy of mixing and the ξ-values at 670 and 720 K in the whole range of composition. A number within parenthesis is the estimated standard deviation (esd). The accuracy obtained is 1% for $\Delta_m H^\circ$ at 670 K and 0.6% for $\Delta_m H^\circ$ at 720 K. The present value is in acceptable agreement with that by Hultgren et al.[5] From curve-fitting calculations, the following polynomial functions for $\Delta_m H$ are derived:

$T = 670$ K;

$$\Delta_m H^\circ = 4.438x_2 - 5.467x_2^2 + 1.029x_2^3, \tag{3}$$

$T = 720$ K;

$$\Delta_m H^\circ = 5.129x_2 - 6.363x_2^2 + 1.224x_2^3. \tag{4}$$

The curve of $\Delta_m H^\circ$ against the composition is shown in Figs. 1 and 2. Figure 2 illustrates the trend of $\Delta_m H^\circ$ at 670 and 720 K. From the data in Table 3 one may conclude that the enthalpy of mixing is small compared with that for other systems e.g. Sn–Sb.[2] This is due to excellent mixing of Pb with In. The enthalpy of mixing is positive and increases with the increase of indium mole fraction to reach a maximum at x_{In}=0.5 (Figs. 1, 2); after that the enthalpy of mixing decreases with the increase of the composition. The partial molar quantities of an integral thermodynamic property, Y, is given by

$$y_1 = Y - x_2 \cdot (\partial Y/\partial x_2)_{T,p} \tag{5}$$

and

$$y_2 = Y - (x_2 - 1) \cdot (\partial Y/\partial x_2)_{T,p} \tag{6}$$

Using Eqs. 3, 4, 5, and 6, we obtain

$T = 670$ K;

$$\Delta_m H_1^\circ = 5.467x_2^2 - 2.058x_2^3, \tag{7}$$

Table 2. Enthalpy Differences of the PbIn Alloys in kJ mol^{-1}. M(Pb)=207.2 g mol^{-1}; M(In)=114.82 g mol^{-1}

x_{In}	H_3°(670 K)–H_3°(298.15 K)	H_3°(720 K)–H_3°(423 K)
0.600	25.861	21.950
0.650	25.866	21.940
0.700	25.862	21.917
0.750	25.872	21.914

Table 3. Integral and Partial Molar Enthalpies of Mixing; ξ-Values in the System Lead–Indium in kJ mol^{-1}. Estimated Standard Deviations in Parenthesis. M(Pb)=207.2 g mol^{-1}; M(In)=114.82 g mol^{-1}

x_{In}	T=670 K				T=720 K			
	$\Delta_m H^\circ$	$\Delta_m H_1^\circ$	$\Delta_m H_2^\circ$	ξ	$\Delta_m H^\circ$	$\Delta_m H_1^\circ$	$\Delta_m H_2^\circ$	ξ
0.000	0	0	4.438	4.438	0	0	5.129	5.129
0.100	0.390(6)	0.034	3.428	4.335	0.447(4)	0.061	3.956	5.007
0.200	0.669(8)	0.202	2.577	4.232	0.776(5)	0.235	2.969	4.884
0.300	0.859(8)	0.436	1.871	4.129	1.005(5)	0.506	2.153	4.762
0.400	0.957(9)	0.743	1.301	4.026	1.109(5)	0.860	1.494	4.639
0.500	0.972(9)	1.110	0.852	3.924	1.135(6)	1.282	0.976	4.517
0.600	0.899(8)	1.524	0.513	3.821	1.051(4)	1.758	0.586	4.395
0.700	0.781(7)	1.973	0.272	3.718	0.892(4)	2.273	0.307	4.272
0.800	0.578(9)	2.445	0.112	3.615	0.670(6)	2.813	0.127	4.150
0.900	0.308(8)	2.928	0.026	3.512	0.365(3)	3.361	0.029	4.027
1.000	0	3.409	0	3.409	0	3.905	0	3.905

$$\Delta_m H_2^\circ = 4.438 - 10.934x_2 + 8.554x_2^2 - 2.058x_2^3. \quad (8)$$

$T = 720$ K;

$$\Delta_m H_1^\circ = 6.353x_2^2 - 2.448x_2^3, \quad (9)$$

$$\Delta_m H_2^\circ = 5.129 - 12.706x_2 + 10.025x_2^2 - 2.448x_2^3. \quad (10)$$

Table 3 also illustrates the ξ-values. For ξ (T), the following equation was used:

$$\xi(T) = \Delta_m H^\circ(T)/x_2 \cdot (1 - x_2). \quad (11)$$

The polynomial functions for $\Delta_m H^\circ(T)$ were employed together with Eq. 11 to derive the following relations for ξ:

$$\xi(670\,\mathrm{K}) = 4.438 - 1.029x_2, \quad (12)$$

$$\xi(720\,\mathrm{K}) = 5.129 - 1.224x_2. \quad (13)$$

With reference to these equations, $\xi(T)$ exhibits a linear function. Figure 3 represents the experimentally determined values for ξ.

(iii) Enthalpy of Formation. The enthalpy of formation is the special form of the enthalpy of reaction evolved by the formation of the substance from the elements. In the case of lead-indium alloy, the formation reaction is

$$-(1 - x_2)\cdot \mathrm{Pb}(\mathrm{s}, T_0) - x_2 \cdot \mathrm{In}(\mathrm{s}, T_0) + \mathrm{Pb}_{1-x_2}\mathrm{In}_{x_2}(\mathrm{s}, T_0) = 0 \quad (14)$$

where T_0 is the intial temperature.

The enthalpy of formation is then

$$\Delta_f H^\circ = -(1 - x_2)\cdot H_1^\circ(T_0) - x_2 \cdot H_2^\circ(T_0) + H_3^\circ(T_0) \quad (15)$$

The indices 1, 2, and 3 indicate lead, indium, and the alloy, respectively.

Subtraction of Eq. 15 from Eq. 2, yields

$$\Delta_m H^\circ - \Delta_f H^\circ = -(1 - x_2)\cdot[H_1^\circ(T_1) - H_1^\circ(T_0)] - x_2 \cdot [H_2^\circ(T_1) - H_2^\circ(T_0)] + [H_3^\circ(T_1) - H_3^\circ(T_0)]. \quad (16)$$

The term $[H_3^\circ(T_1) - H_3^\circ(T_0)]$ which appears in Eq. 16 is the enthalpy difference of the alloy; this was measured between 298.15 and 670 K; between 423 and 720 K. The enthalpy differences $[H_1^\circ(T) - H_1^\circ(T_0)]$ and $[H_2^\circ(T) - H_2^\circ(T_0)]$ are measured accurately (see Table 1).

The following schema illustrates the above given procedure for determining of $\Delta_f H^\circ$:

$$\begin{tikzcd}
\mathrm{Pb}(l,T) \arrow[r, "\Delta_m H^\circ"] & {} \arrow[d, "H_3^\circ"] & \mathrm{In}(l,T) \arrow[l] \\
\mathrm{Pb(s)} \arrow[u, "H_1^\circ"] \arrow[r] & \mathrm{PbIn} & \mathrm{In(s)} \arrow[l, "\Delta_f H^\circ"'] \arrow[u, "H_2^\circ"']
\end{tikzcd}$$

The non-measurable process of the enthalpy of formation will be substituted by (1) heating of lead and indium at T_1, (2) measurement of the enthalpy of mixing at T_1, and (3) measurement of the enthalpy difference of the single miscible phase between T_0 and T_1. Employing this procedure, the enthalpy of formation at 298.15 and 423 K has been determined at four compositions.

The integral and partial molar enthalpies of formation at 298.15 and 423 K are presented in Table 4 for four compositions. A number within parenthesis is the estimated standard deviation (esd). The average error of the individual measurement was found to be 0.2% for T=298.15 K and 0.3% for T=423 K. Using the

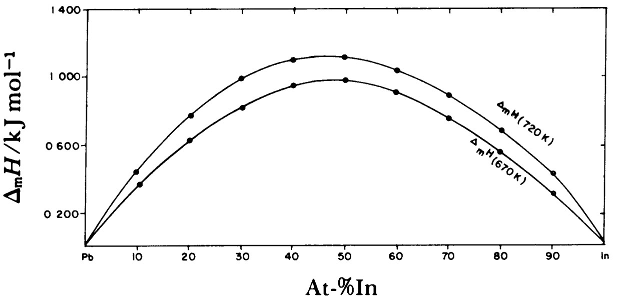

Fig. 3. The enthalpies of mixing at 670 and 720 K in the system Pb-In.

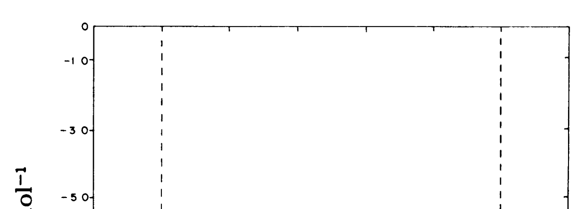

Fig. 4. The ξ-function at 670 and 720 K in the system Pb-In.

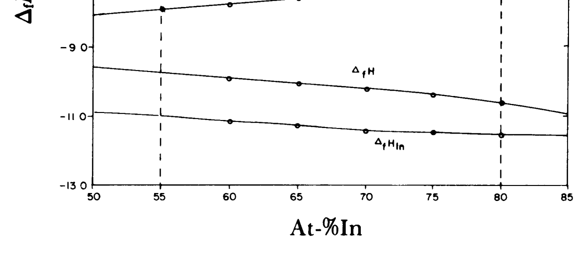

Fig. 5. The integral and partial molar enthapies of formation at 298.15 K in the system Pb-In.

Table 4. Integral and Partial Molar Enthalpy of Formation of the β-Phase in the System Lead–Indium in kJ mol^{-1}. Estimated Standard Deviations in Parenthesis. M(Pb)=207.2 g mol^{-1}; M(In)=114.82 g mol^{-1}

x_{In}	T=298.15 K			T=423 K		
	$-\Delta_f H^\circ$	$-\Delta_f \bar{H}_1^\circ$	$-\Delta_f \bar{H}_2^\circ$	$-\Delta_f H^\circ$	$-\Delta_f \bar{H}_1^\circ$	$-\Delta_f \bar{H}_2^\circ$
0.600	9.868(18)	7.827	11.228	8.081(21)	6.426	9.219
0.650	10.044(1)	7.642	11.339	8.247(1)	6.247	9.310
0.700	10.227(10)	7.442	11.517	8.628(14)	6.110	9.389
0.750	10.444(28)	7.227	11.517	8.628(53)	5.933	9.456

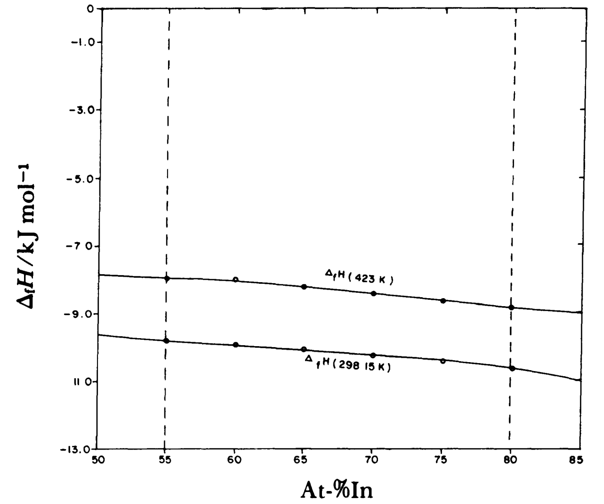

Fig. 6. The enthalpies of formation at 298.15 and 423 K in the system Pb–In.

data in Table 4, it was possible to derive equations which produce the curves shown in Fig. 5 as follows:

$$\Delta_f H^\circ(298.15\,\mathrm{K}) = -8.886 + 0.119x_2 - 2.908x_2^2 - 0.028x_2^3, \tag{17}$$

$$\Delta_f H^\circ(423\,\mathrm{K}) = -7.296 + 0.098x_2 - 2.388x_2^2 - 0.023x_2^3. \tag{18}$$

It is apparent that the enthalpy of formation displays a somewhat pronounced temperature dependence. However, it appears that $\Delta_f H^\circ$ in other systems e.g. Al–Zn[6] exhibits larger temperature dependence.

The enthalpy of formation in the system Pb–In is negative and becomes more negative at higher composition. This is due to the insertion of the smaller indium atom in the structure of PbIn which becomes more stable at higher mole fraction of indium.

With reference to the definitions of the partial quantities (Eqs. 5 and 6), and using Eqs. 17 and 18, the following equations for $\Delta_f \bar{H}_1^\circ$ and $\Delta_f \bar{H}_2^\circ$ are derived:

$T = 298.15$ K;

$$\Delta_f \bar{H}_1^\circ = -8.886 + 2.908x_2^2 + 0.056x_2^3, \tag{19}$$

$$\Delta_f \bar{H}_2^\circ = -8.767 - 5.816x_2 + 2.824x_2^2 + 0.056x_2^3. \tag{20}$$

$T = 423$ K;

$$\Delta_f \bar{H}_1^\circ = -7.296 + 2.388x_2^2 + 0.046x_2^3, \tag{21}$$

$$\Delta_f \bar{H}_2^\circ = -7.198 - 4.776x_2 + 2.319x_2^2 + 0.046x_2^3. \tag{22}$$

The curve in Fig. 4 shows that the partial enthalpy of formation of lead is negative but increases at higher composition. However, $\Delta_f \bar{H}_1^\circ$ is always negative. This means that the structure remains stable even when the composition increases. The partial molar enthalpy of formation of indium is also negative and becomes more negative at higher composition. For a heteropolar behavior, the delivery of electrons from indium to lead would increase with the increase of indium mole fraction so that the partial molar enthalpy of formation of indium should increase with the increase of the composition.

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