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HEAT OF FORMATION OF SOLID INDIUM-LEAD ALLOY

Hong Il Yoon

(M.S. Thesis)

September, 1968

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HEAT OF FORMATION OF SOLID INDIUM-LEAD ALLOY

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September, 1968

ABSTRACT

The heats of formation at 315°K of solid indium-lead alloys of composition $X_{\text{Pb}} = 0.1 - 0.9$ have been measured by means of liquid tin solution calorimetry. The alloys are endothermic except that for the α -phase, $\Delta H_f = 0(\pm 40)$ cal/g-atom. The partial molar heats of solution of In and Pb in liquid tin at 650°K were also determined.

I. INTRODUCTION

Indium and lead form wide-ranging solid solutions in each other with a single intermediate phase, β . The liquidus and solidus have been fairly well determined,^{1,2} but the boundaries of the solid phases have not been studied in detail. The phase diagram is given in Figure 1.

The crystal structures of the three solid phases are rather similar. Lead has a face-centered-cubic structure isotypic with copper. Indium has the same structure except the c-axis is elongated about 7.6%, making it face-centered-tetragonal. The β phase is also face-centered-tetragonal, but the c-axis is shorter than the a-axis by about 7%.

The thermodynamic properties of the liquid phase are fairly well established,³ but for the solid phases the only studies seem to be differential-thermal-analysis determinations of the heats of formation.⁴ Since this method is not well proved for quantitative accuracy, it was decided to determine the heats of formation by liquid tin solution calorimetry.

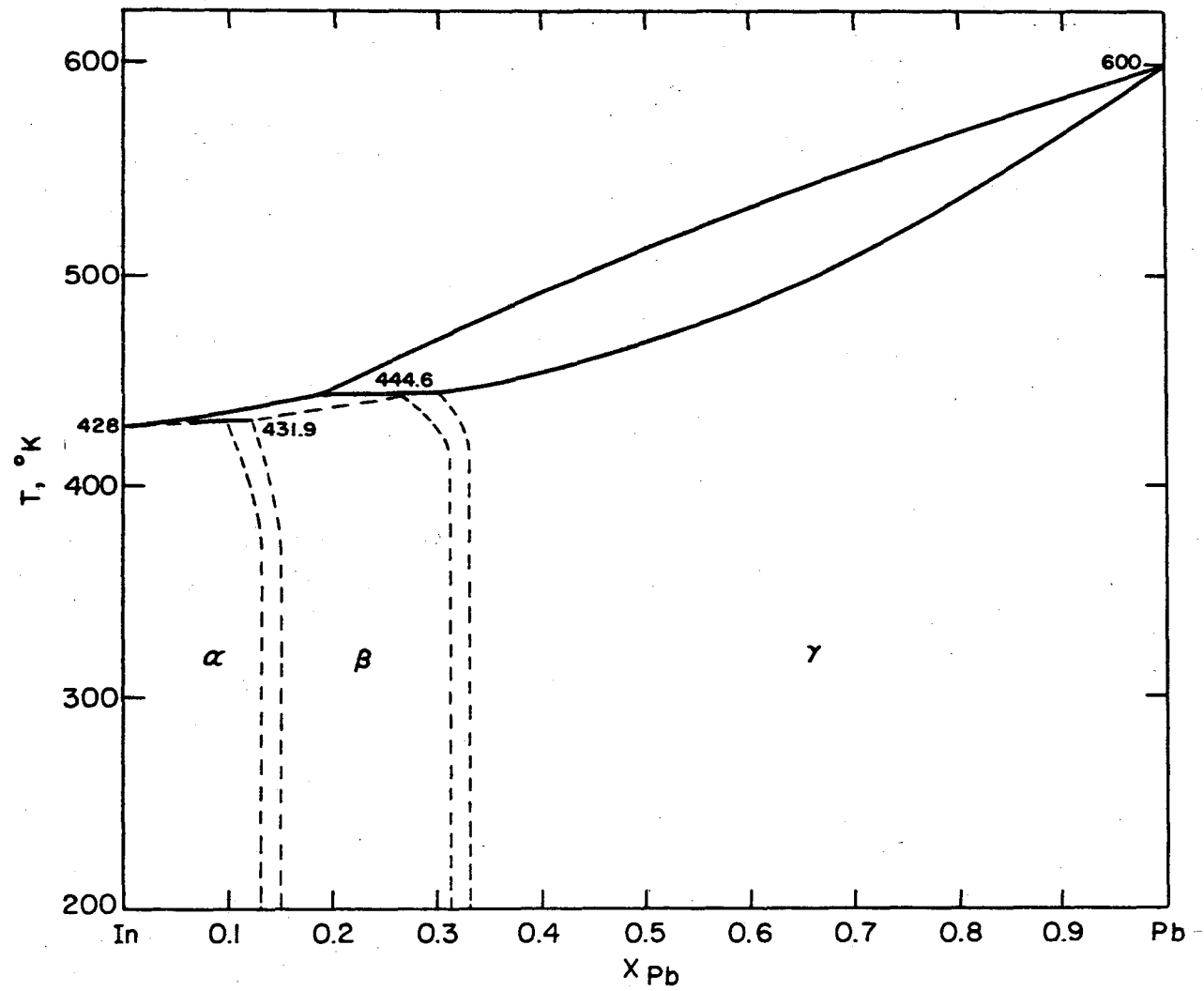


FIG. 1 Phase Diagram for In-Pb System

II. EXPERIMENTAL PROCEDURE

Preparation of Alloys

The tin used for the experiment was obtained from the Vulcan Detinning Company, Sewaren, New Jersey; the lead, from the American Smelting and Refining Company, South Plainfield, New Jersey; and the indium, from the Cominco Electronics, Inc., Spokane, Washington. Each was reported to be 99.999% pure.

Nine indium-lead alloys, approximately twelve grams each, were prepared. The metals were melted together at about 20°C higher than the liquidus temperatures in sealed Pyrex tubes containing an atmosphere of helium with 4% hydrogen. The alloys were shaken during the melting to assure complete mixing and then quenched in ice water to decrease segregation. They were weighed before and after the melting and showed no loss within the experimental error. The ingots were cold worked to aid diffusion and homogenized for seven days at about 10°- 15°C below the solidus temperature.

X-ray Analysis

Filings were taken from both ends of the ingots and strain annealed in boiling water for fifteen minutes in evacuated Pyrex tubes. An X-ray diffractometer using Cu-K_α radiation was used to examine the homogeneity of the alloys. Back reflection diffraction lines showed sharp peaks of the Cu-K_α doublets indicating they were homogeneous. The

lattice constants were calculated from the diffraction angles and found to agree well with previous measurements.^{4, 5}

Calorimetry

A liquid tin solution calorimeter was used in the experiments. A complete description of the apparatus has been given in detail previously.⁶ A schematic drawing of the calorimeter is given in Figure 2. From a nickel dispenser where the sample is held at 315°K, alloys and pure metals (spherical shape 0.5 mm in diameter; 0.002- 0.003 g-atom of sample) were dropped into the liquid tin bath (about 2.1 g-atom of tin) at a temperature of 650°K. The change of temperature of the tin bath (actually the difference of the temperature between the tin bath and the surrounding copper jacket) due to the dissolving of the sample was measured by a differential copper-constantan thermocouple by means of a potentiometer whose sensitivity was such that a scale deflection of 1 mm. corresponded to change of about $0.15 \mu\text{v}$ or 0.00024°C . The system was evacuated to about 10^{-6} mm Hg in order to prevent the sample from oxidizing, to eliminate temperature disturbances due to convection, and to cut down the rate of heat transfer between the tin bath and the jacket. The tin bath was stirred during a run by a molybdenum impeller attached to an alundum shaft. The temperature of the jacket was held constant by a controller which kept the temperature constant within about 0.001°C . The method of evaluation of data has

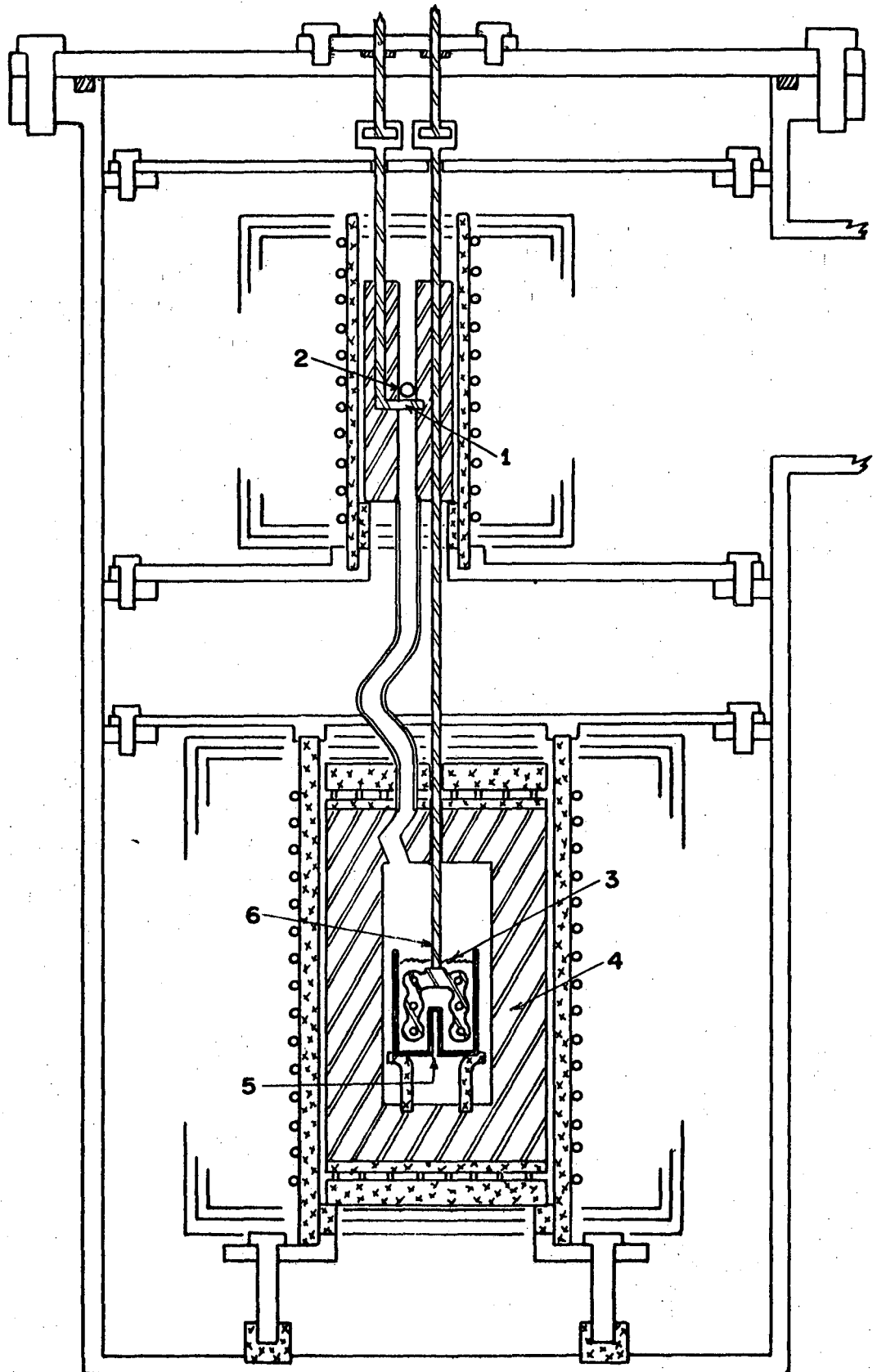


FIG. 2 Liquid Tin Solution Calorimeter

Schematic Drawing of the Liquid Tin Solution Calorimeter

- 1: Dispenser
- 2: Sample
- 3: Liquid Tin Bath
- 4: Copper Jacket
- 5: Thermocouple Well
- 6: Molybdenum Impeller on Alundum Shaft

been described.⁶ The heat capacity of the calorimeter was determined by dropping samples of solid tin of known weight to the liquid tin bath at the beginning and the end of a series of runs. The concentration of the impurities (indium and lead) in the tin solution at the end of each series was about 1.5 atomic percent.

III. CALCULATIONS AND RESULTS

The heat of formation of the alloy at the initial temperature T_i was obtained by subtracting the heat of solution of the alloy from the heat of solution of corresponding amount of the pure metals as follows:

$$(1) \text{ In (s, } T_i) = \text{ In (l, Sn sol'n, } T_f) - \dots - \Delta H_1$$

$$(2) \text{ Pb (s, } T_i) = \text{ Pb (l, Sn sol'n, } T_f) - \dots - \Delta H_2$$

$$(3) \text{ In}_{1-x}\text{Pb}_{1-x} \text{ (s, } T_i) = (1-x)\text{In (l, Sn sol'n, } T_f) + x \text{ Pb (l, Sn sol'n, } T_f) - \dots - \Delta H_3$$

(1-x) equation (1) + x equation (2) - equation (3) gives

$$(1-x)\text{In(s, } T_i) + x \text{ Pb(s, } T_i) = \text{ In}_{1-x}\text{Pb}_x \text{ (s, } T_i) - \dots - \Delta H_{f, T_i}$$

Therefore $\Delta H_{f, T_i} = (1-x)\Delta H_1 + x\Delta H_2 - \Delta H_3$. The heats of solution of the pure metals in tin at the final solution temperature T_f are presented in Table I. The heat contents of tin, indium, and lead were taken from the values of Hultgren, et al.³ in order to calculate the heats of solution of the pure metals. These data give the partial molar heats of solution at 650°K in pure tin as follows:

$$\overline{\Delta H}_{\text{In}}^0 = -167 \text{ cal/g-atom}$$

$$\overline{\Delta H}_{\text{Pb}}^0 = 1410 \text{ cal/g-atom.}$$

The measured heats of solution of the alloys and the calculated heats of formation are presented in Table II. To determine the smoothed integral heat of formation through the measured values, a Q function, defined as $Q = \Delta H_f/x(1-x)$, was plotted against the atomic fraction of Pb.

TABLE I

Heats of Solution of Pure Metals in Sn at 650°K

Run No.	T_i (°K)	T_f (°K)	$\Delta\bar{H}_{i, T_f \text{ in Sn}}^0$ (cal/g-atom)
142-5-Pb1	313.83	648.0	1402
142-3-Pb2	313.3	648.1	1410
144-4-Pb1	314.4	650.4	1419
144-15-Pb2	313.8	650.6	1420
145-4-Pb1	314.6	650.2	1406
145-12-Pb2	314.6	650.2	1393
146-4-Pb1	314.1	649.8	1436
146-10-Pb2	314.5	649.6	1391
142-6-In1	313.8	648.0	-188
142-14-In2	313.2	647.9	-176
144-3-In1	314.2	650.4	-149
144-16-In2	313.8	650.6	-160
145-3-In1	314.2	649.7	-171
145-14-In2	314.4	650.2	-172
146-3-In1	314.5	649.8	-163
146-10-In2	314.5	649.7	-161

TABLE II

Experimental Values of Heats of Formation

Run No.	Composition	T_i (°K)	T_f (°K)	$\Delta H_{\text{sol'n, alloy}}^{\text{sol'n, alloy}}$ $T_i \rightarrow T_f$ (cal/g-atom)	$\Delta H_{f, T_i}$ (cal/g-atom)
142-12	Pb _{.1} In _{.9}	313.0	648.0	3080	43
145-5	Pb _{.1} In _{.9}	314.2	650.0	3147	-18
145-17	Pb _{.1} In _{.9}	314.2	650.3	3136	-5
146-5	Pb _{.1} In _{.9}	314.1	649.8	3170	-42
142-10	Pb _{.2} In _{.8}	313.3	648.1	3118	191
144-8	Pb _{.2} In _{.8}	313.8	650.6	3123	199
145-10	Pb _{.2} In _{.8}	314.4	650.0	3162	154
146-8	Pb _{.2} In _{.8}	314.7	649.8	3124	188
142-8	Pb _{.3} In _{.7}	313.3	648.1	3219	279
144-6	Pb _{.3} In _{.7}	314.0	650.6	3251	257
145-9	Pb _{.3} In _{.7}	314.2	650.0	3235	270
146-9	Pb _{.4} In _{.6}	314.5	649.7	3384	306
142-7	Pb _{.5} In _{.5}	313.3	648.1	3554	321
144-5	Pb _{.5} In _{.5}	314.4	650.3	3588	296
145-6	Pb _{.5} In _{.5}	314.8	650.0	3576	303
146-7	Pb _{.6} In _{.4}	314.5	649.7	3792	275
142-9	Pb _{.7} In _{.3}	313.3	648.1	4002	251
145-7	Pb _{.7} In _{.3}	313.8	650.0	4021	241
144-9	Pb _{.8} In _{.2}	314.0	650.5	4270	182
145-11	Pb _{.8} In _{.2}	315.1	650.0	4249	193
142-14	Pb _{.85} In _{.15}	313.2	648.0	4367	169
144-11	Pb _{.85} In _{.15}	314.0	650.6	4415	131
142-11	Pb _{.9} In _{.1}	313.0	648.1	4569	63
144-7	Pb _{.9} In _{.1}	314.2	650.6	4601	41
145-8	Pb _{.9} In _{.1}	313.8	650.0	4532	107
146-6	Pb _{.9} In _{.1}	314.1	649.7	4544	91

From the smoothed Q function the integral heats of formation were obtained. The integral heats of formation as well as Q function vs atomic fraction of Pb are shown in Figure 3. These values are compared with those of Heumann and Predel⁴ in Figure 4. The heat of formation of the α -phase is approximately zero, the value for an ideal solution. In the β -phase the Q function was found to be $Q = 1070 + 700x$. The selected values of Q function also provide a simple accurate way of determining the partial molal heats of two components.

$$\Delta \bar{H}_x = \Delta H + (1-x) (d\Delta H/dx)$$

$$= (1-x)^2(Q + x dQ/dx),$$

and $\Delta \bar{H}_{1-x} = x^2 \left(Q - (1-x) dQ/dx \right)$. In the β -phase

$$\Delta \bar{H}_{Pb} = (1-x)^2(1070 + 1400 x)$$

$$\Delta \bar{H}_{In} = x^2(370 + 1400 x). \text{ In particular, when } x_{In} = 0, \Delta \bar{H}_{In}^0 \text{ (the}$$

relative partial molar enthalpy of In in its infinitely dilute solution in Pb) = Q. Hence, $\Delta \bar{H}_{In, x_{Pb} = 1}^0 = 1150 \text{ cal/g-atom}$. The partial molar heats of the components are shown in Figure 5.

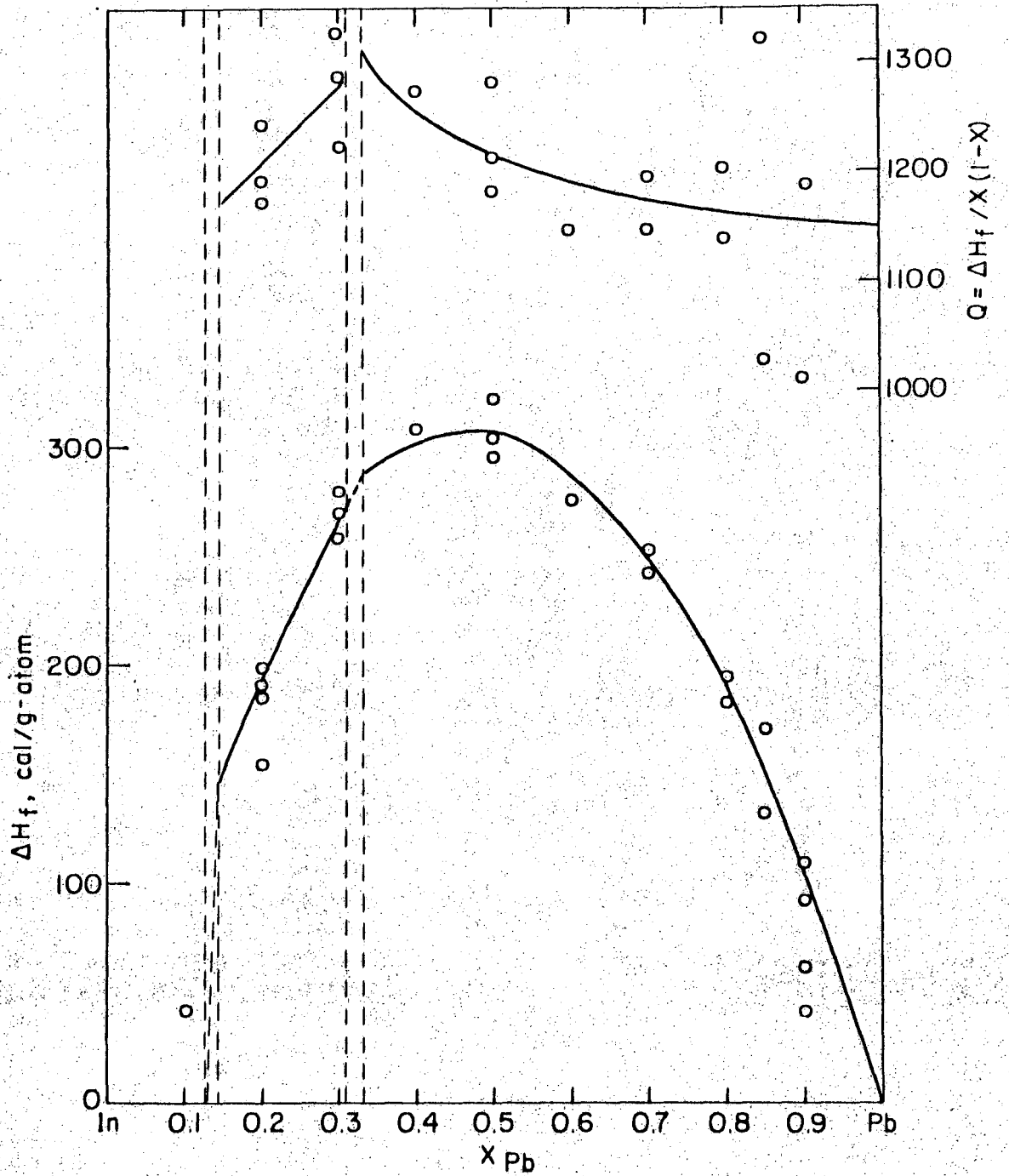


FIG. 3 Heats of Formation and Q Functions of the Alloys at 315°K

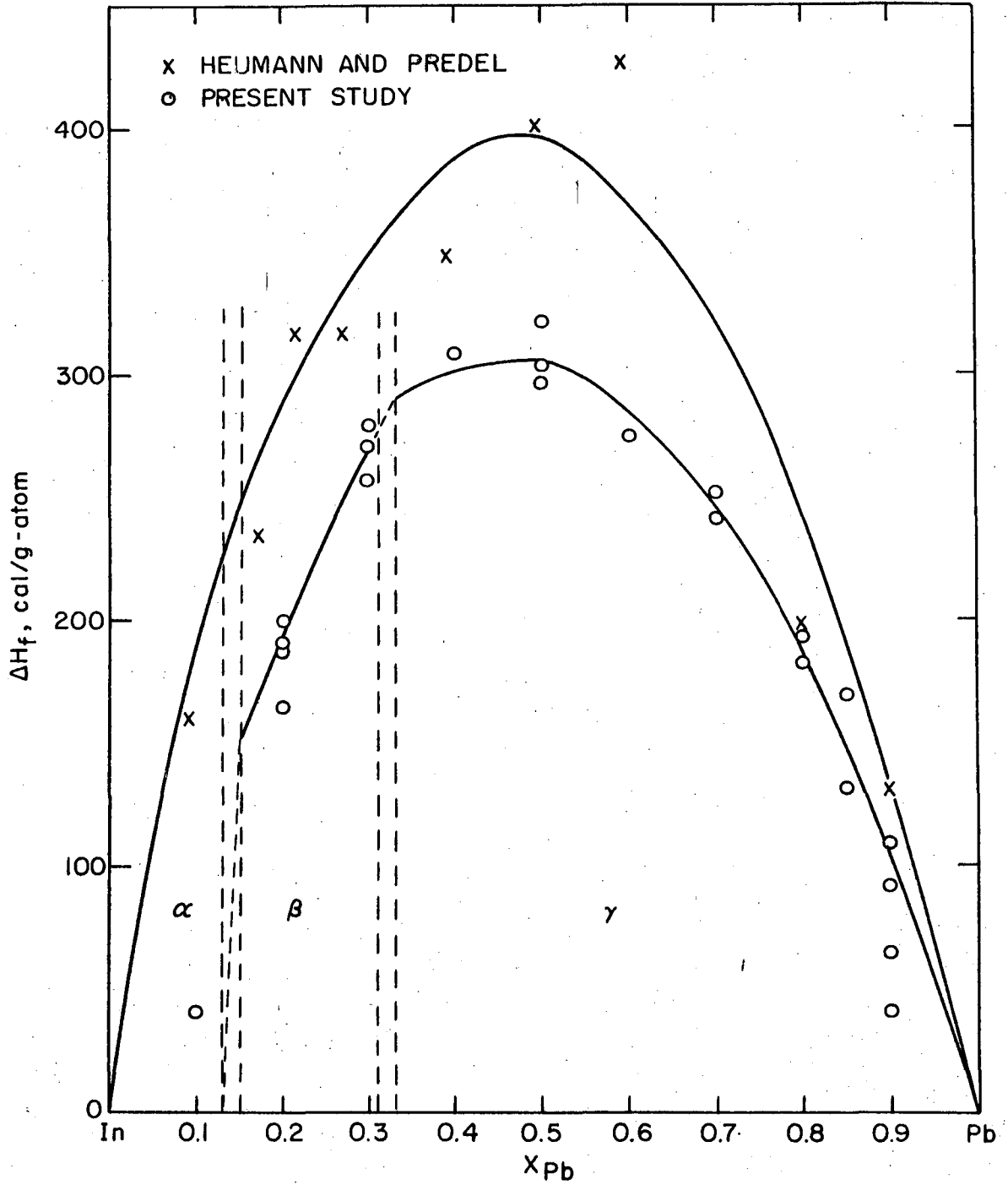


FIG. 4 Heats of Formation of In-Pb Alloys at 315°K.

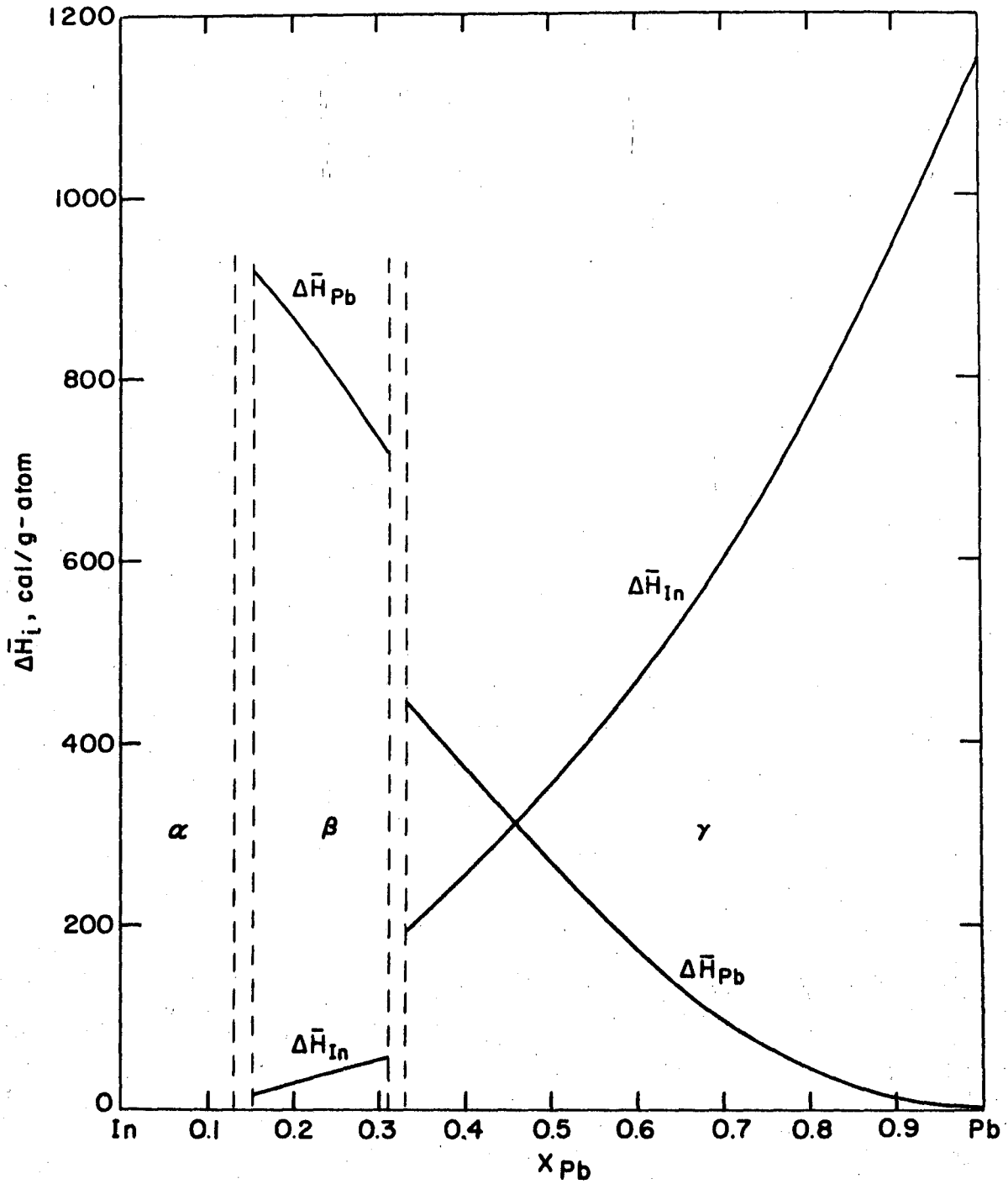


FIG. 5 Partial Molar Heats of Formation of In-Pb Alloys at 315°K.

IV. DISCUSSION

Previously determined partial molar heats of solution in pure liquid tin are in reasonable agreement with present values, but tend to be slightly more endothermic. For indium Orr⁷ found $\Delta\bar{H}_{\text{In}}^{-0} = -203 \text{ cal/g-atom}$, at 705°K, compared with -167 found in the present work. For lead Kleppa⁸ found $\Delta\bar{H}_{\text{Pb}}^{-0} = 1360 \text{ cal/g-atom}$ at 623° and 723°K compared with the present value, 1410 at 650°K.

Heumann and Predel's⁴ more endothermic heats of formation were obtained in the following way. By the DTA apparatus they measured enthalpies of melting of the pure components and the alloys. The differences of these heats were added to the literature values for heats of formation in the liquid state to get the heats of formation in the solid state. This neglects any deviations from Kopp's law in the liquid or solid alloys. Scheil and Lukas⁹ found for a liquid alloy of composition $x_{\text{Pb}} = 0.55$, that the heat of formation increased by 30 cal/g-atom between the temperatures of 523° and 823°K; hence, $\Delta C_p = 0.1 \text{ cal/g-atom deg}$. Such deviations would make Heumann and Predel's heats of formation in the solid state too endothermic, accounting for at least part of the moderate disagreement.

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