Title

I CALORIMETRIC DETERMINATION OF SOLUTE-SOLUTE INTERACTIONS IN SOME DILUTE TIN-RICH LIQUID ALLOYS

Author

Orr, Raymond L.

Publication Date

1966-03-01

UCRL-16320 Rev. 1

University of California

Ernest O. Lawrence Radiation Laboratory

CALORIMETRIC DETERMINATION OF SOLUTE-SOLUTE INTERACTIONS IN SOME DILUTE TIN-RICH LIQUID ALLOYS

Berkeley, California

Trans. Met. Soc. 1966 Ann. AIME

UCRL-16320 Rev. 1

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

AEC Contract W-7405-eng-48

CALORIMETRIC DETERMINATION OF SOLUTE-SOLUTE INTERACTIONS IN SOME DILUTE TIN-RICH LIQUID ALLOYS

Raymond L. Orr

March 1966

Calorimetric Determination of Solute-Solute Interactions in Some Dilute Tin-Rich Liquid Alloys

Raymond L. Orr

Abstract

Calorimetric measurements have been made of the heats of solution of gold and indium in a number of liquid tin-rich alloys at a temperature of 705° K. Partial molar enthalpies of gold were determined as a function of dilute solute concentrations in the binary Au-Sn system and in the ternary Ag-Au-Sn and Au-In-Sn systems. Partial molar enthalpies of indium were determined for dilute solute concentrations in the In-Sn, Ag-In-Sn, and Au-In-Sn systems.

Through application of the interaction coefficient concept introduced by Wagner and more recently extended by Lupis and Elliott, values have been obtained for the gold-gold, silver-gold, gold-indium, and silver-indium enthalpy interaction coefficients in liquid tin. The results are interpreted in terms of solute atom distributions through comparisons with the predictions of dilute solution models.

Raymond L. Orr, Member AIME, is Research Metallurgist, Inorganic Materials Research Division, Lawrence Radiation Laboratory, and Department of Mineral Technology, College of Engineering, University of California, Berkeley, California.

Interest in the thermodynamic behavior of dilute liquid alloys stems from two primary sources. From a practical viewpoint, it is often of importance to know or to be able to predict the effect that one solute will have on the thermodynamic properties of the other solutes in a multicomponent system. Studies of dilute solutions may also be rewarding from the theoretical point of view. Some of the difficulties arising from the more complex interactions possible in concentrated solutions are avoided, leading to easier interpretations in terms of solution models and bonding energies. For example, in a binary alloy the limiting values of the partial molar properties of the solute represent the case for which each solute atom is completely surrounded by atoms of the solvent, and no other interactions are possible.

Solute-solute interactions in dilute solutions are conveniently treated by the interaction coefficient concept of Wagner.[1] Using a Taylor series expansion for the logarithm of the activity coefficient, $\ln \gamma_i$, of a component, _i_, in a solution consisting of dilute solutes with atomic fractions x_i, x_j, x_k, etc., in a solvent, _s_, and neglecting the second- and higher-order terms, Wagner obtained the expression:

$$\ln \gamma_i = \ln \gamma_i^\circ + x_i \epsilon_i^i + x_j \epsilon_i^j + x_k \epsilon_i^k + \cdots \tag{1}$$

where γ_i° is the limiting value of γ_i in the pure solvent, _s_. The interaction coefficients, ϵ_i^i, ϵ_i^j, etc., are defined by:

$$\epsilon_i^i = \left(\frac{\partial \ln \gamma_i}{\partial x_i} \right)_{x_s = 1}, \qquad \epsilon_i^j = \left(\frac{\partial \ln \gamma_i}{\partial x_j} \right)_{x_s = 1}, \quad \text{etc.} \tag{2}$$

Since γ_i is related to the excess partial molar Gibbs energy of component $\underline{i}$ by $\Delta\overline{G}_i^{xs} = RT\ln\gamma_i$, ϵ_i^j is referred to as the "Gibbs energy interaction coefficient."

Lupis and Elliott[2] extended Wagner's treatment to the partial molar enthalpy, $\Delta\overline{H}_i$, and the excess partial molar entropy, $\Delta\overline{S}_i^{xs}$. They defined the enthalpy interaction coefficient as:

$$\eta_i^j = \left(\frac{\partial\,\Delta\overline{H}_i}{\partial x_j}\right)_{x_s = 1} , \tag{3}$$

and the excess entropy interaction coefficient as:

$$\sigma_i^j = \left(\frac{\partial\,\Delta\overline{S}_i^{xs}}{\partial x_j}\right)_{x_s = 1} , \tag{4}$$

leading to expressions similar to Eq. (1):

$$\Delta\overline{H}_i = \Delta\overline{H}_{i\,(x_s = 1)} + x_i\eta_i^i + x_j\eta_i^j + \cdots \tag{5}$$

$$\Delta\overline{S}_i^{xs} = \Delta\overline{S}_i^{xs}\,(x_s = 1) + x_i\sigma_i^i + x_j\sigma_i^j + \cdots \tag{6}$$

The three interactions coefficients are related by:[2]

$$RT\,\epsilon_i^j = \eta_i^j - T\sigma_i^j \tag{7}$$

The self-interaction coefficients, ϵ_i^i, η_i^i, and σ_i^i, represent the effects of interactions between atoms of component $\underline{i}$; ϵ_i^j, η_i^j, and σ_i^j represent the effects of interactions between $\underline{i}$ and $\underline{j}$ atoms, etc. From the usual Maxwell-type relationships between partial molar quantities, it may be shown[1, 2] that $\epsilon_i^j = \epsilon_j^i$, $\eta_i^j = \eta_j^i$, and $\sigma_i^j = \sigma_j^i$.

Experimental determination of the interaction coefficients requires extremely precise measurements of the appropriate properties as functions of solute concentrations in very dilute regions. Few such data exist for intermetallic alloys, even for binary systems, because of experimental difficulties. This is especially true with respect to enthalpy data for dilute alloys. Examination of the compilation of data for binary alloys by Hultgren, Orr, Anderson, and Kelley[3] reveals that determination of limiting values of $\Delta\overline{H}_{i\,(x_i=0)}$ often requires extrapolations to infinite dilution from $x_i \approx 0.05 - 0.10$.

Direct measurements of the enthalpy interaction coefficient, η_i^j, for multicomponent systems are virtually nonexistent. This quantity is of course subject to direct calorimetric measurement, but its determination must be limited to cases where high experimental precision is possible. The heats of solution of gold and indium in liquid tin can be measured with relatively high precision, which makes determinations of η_i^j involving these metals as the measured solutes experimentally attractive. This paper presents the results of such determinations of the gold-gold, silver-gold, gold-indium, and silver-indium enthalpy interaction coefficients in liquid tin.

MODELS FOR DILUTE SOLUTION BEHAVIOR

Random Solution Behavior. In the quasi-chemical treatment of solutions, only nearest neighbor bonds are considered, and a composition independent value is assumed for the pairwise interaction energy term:

$$V_{ij} = E_{ij} - \tfrac{1}{2}(E_{ii} + E_{jj}) \qquad (8)$$

where E_{ij} is the energy of an i-j bond, etc. The so-called "zeroth" approximation[4] of this treatment, referred to throughout this paper as the "random solution model", further assumes random mixing of the component atoms. Based on this model, the partial molar enthalpy of component i in a binary alloy is given by:[4]

$$\Delta\overline{H}_i = N_o z V_{ij} (1-x_i)^2 \qquad (9)$$

where N_o is Avogadro's number and z is the coordination number, assumed to be the same for the pure components and the alloy. In the infinitely dilute solution of i in j, the limiting value of $\Delta\overline{H}_i$ is given by:

$$\Delta\overline{H}_{i(x_j=1)} = N_o z V_{ij} \qquad (10)$$

and the enthalpy self-interaction coefficient for solute i, by:

$$\eta_i^i = \left(\frac{\partial \Delta\overline{H}_i}{\partial x_i}\right)_{x_j=1} = -2N_o z V_{ij} = -2\Delta\overline{H}_{i(x_j=1)} \qquad (11)$$

The quasi-chemical assumption that V_{ij} does not vary with composition is not generally valid for intermetallic systems as shown by the fact that the limiting partial molar enthalpies in a given liquid binary alloy system usually differ, sometimes by considerable amounts.[3] Nevertheless, over a small range of composition such as in the very dilute range for one of the components, the assumption that V_{ij} is constant should be reasonably valid. Therefore for component i in very dilute solution in j, a departure from the behavior predicted by Eq. (11) could be concluded to result primarily from a non-random distributiom of the solute atoms.

By applying the zeroth approximation assumptions to a liquid ternary alloy, Alcock and Richardson[5] derived the following equation for the enthalpy interaction coefficient of dilute components i and j in solvent metal s:

$$\eta_i^j = \left(\frac{\partial \Delta \overline{H}_i}{\partial x_j}\right)_{x_s=1} = \Delta \overline{H}_i \, (\text{in } j)_{x_j=1} - \Delta \overline{H}_i \, (\text{in } s)_{x_s=1} - \Delta \overline{H}_j \, (\text{in } s)_{x_s=1} \qquad (12)$$

where the three terms on the right hand side of the equation represent the limiting partial molar enthalpies in the three respective binary alloys. The last two terms are unambiguously evolved in the treatment, since metal s is the major component for the binary systems they represent as well as for the ternary alloy. The term, $\Delta \overline{H}_i \, (\text{in } j)_{x_j=1}$, however, evolves from the expression, $N_o z V_{ij}$, which according to the model employed could just as well be given by $\Delta \overline{H}_j \, (\text{in } i)_{x_i=1}$. Thus in calculating the value of η_i^j predicted by this model in cases where the values of $\Delta \overline{H}_{i\,(x_j=1)}$ and $\Delta \overline{H}_{j\,(x_i=1)}$ for the binary i - j system are different, it would appear better to use an average of the two limiting values. From Eq. (12) the enthalpy self-interaction coefficient for the ternary alloy is again given by:

$$\eta_i^i = -2\Delta \overline{H}_i \, (\text{in } s)_{x_s=1} \qquad (13)$$

For the very dilute range of solutes i and j in solvent s, the assumption that the interaction energy terms, V_{is}, V_{js}, and V_{ij}, remain constant is not unreasonable. Thus, a departure in the behavior of an actual dilute ternary system from that predicted by Eq. (12) is most likely to result from one or more of the following: (1) a non-random atomic distribution, (2) other than nearest neighbor interactions, or (3) a difference between the value of V_{ij} in the binary i-j and ternary i-j-s systems. Experimental departures from Eq. (12) must therefore be interpreted in terms of these possibilities, taking into account the nature of the systems involved and the direction and magnitude of the departures.

Henry's Law Behavior. Although Henry's law $\left(\frac{a_i}{x_i} = \text{constant} = \gamma_i^\circ\right)$ is strictly a limiting law for dilute solute behavior, it is sometimes obeyed within experimental precision or closely approached over a finite range of composition. The model deduced from Henry's law behavior for finite solute concentrations in a binary solution is one of a nonrandom atomic distribution for which there are no interactions between solute atoms.* Thus for a dilute binary solution, over the range that solute i is assumed to obey Henry's law, $\Delta\overline{G}_i^{xs}$, $\Delta\overline{H}_i$, and $\Delta\overline{S}_i^{xs}$ will be constant and equal to their values at $x_i = 0$; therefore, $\epsilon_i^i = 0$, $\eta_i^i = 0$, and $\sigma_i^i = 0$. Likewise, for a dilute multicomponent solution in which solute i is assumed to obey Henry's law, i.e., to interact only with the solvent, all of the solute interaction coefficients involving that solute, ϵ_i^i, ϵ_i^j, η_i^i, η_i^j, etc., will have zero values. Non-zero values of the coefficients thus indicate the deviations from Henry's law arising from the types of solute-solute interactions they represent.

The random solution and Henry's law models for the dilute solution represent limiting types of behavior as far as the nature of the distribution

---

*An exception to this model is provided by the special case of an ideal solution, for which the solute obeys Raoult's law, a special case of Henry's law. In this case, $V_{ij} = 0$, and the solute atoms are randomly distributed.

of the solute atoms is concerned. Thus, while both are idealized, they provide useful bases for the comparison and interpretation of the properties of real dilute solutions. Comparisons of measured values of the enthalpy interaction coefficient with those predicted by the two models should serve as most convenient criteria for making such interpretations.

EXPERIMENTAL

Systems Studied. Liquid tin was the major component for all of the systems studied. The heat of solution of gold was measured for several dilute solute compositions in the binary Au-Sn system and in the ternary Ag-Au-Sn and Au-In-Sn systems. Similar measurements were made of the heat of solution of indium in the In-Sn, Ag-In-Sn, and Au-In-Sn systems. Measurements were made for all of the alloys at a temperature of 705 (±2)° K. The metals used were all reported to be 99.999+ pct pure.

Experimental Procedure. The measurements were made using the liquid metal solution calorimeter and experimental methods described in detail in a previous publication.[6] The calorimeter basically consists of a stirred solvent-metal bath contained in a molybdenum crucible which is supported within a heavy copper jacket. The jacket is heated by a surrounding resistance heating element and is maintained at a constant temperature, within ±0.001° C, by means of a sensitive resistance thermometer temperature controller. The temperature difference between the crucible and jacket is measured by means of a copper-constantan differential thermocouple, and the jacket temperature is measured separately by a calibrated platinum-platinum + 10 pct rhodium couple. The calorimeter is contained in the lower half of a chamber evacuated to a pressure of about 10^{-8} atm. Located in the upper part of the chamber and separated from the calorimeter by several radiation shields is the dispenser unit which holds the solute specimens prior to dropping them into the solvent bath. Specimens are admitted to the dispenser unit through an external vacuum-lock device.

For each series of runs, approximately 250-g of tin (~2.1 g-atoms) was melted under vacuum into the molybdenum crucible, which was then installed in the calorimeter and brought to the solution temperature, 705 (±2)° K. Small spherical specimens of gold and indium, consisting of about 0.003 g-atoms of sample, were used for the measurements. The total heat effect accompanying the solution of a specimen dropped from the temperature of the dispenser unit (~321° K) was determined from the change in the crucible temperature, the measured heat capacity of the calorimeter, and a correction for heat transfer between jacket and crucible during the run, using calculation methods previously described.[6] The heat capacity of the calorimeter was determined at the beginning of and during each series of runs by measuring the temperature change accompanying the addition of specimens of solid tin or tungsten. The known heat effects were obtained from tabulated heat content data for tin[3] and tungsten.[7] Solute additions for the purpose of changing the composition of the liquid alloy were also made through the dispenser unit.

Treatment of Data. The isothermal heats of solution at the temperature of the liquid alloy were determined from the measured heat effects and the enthalpy increments[3] of gold and indium between the initial specimen and final solution temperatures. The heat of solution per g-atom of solute added is the average partial molar enthalpy, $\Delta\overline{H}_i$, of that solute over the range of composition covered by the liquid alloy during the run. Since the change in composition was quite small, of the order of $\Delta x_i = 0.0012$, the values have been taken to represent the partial molar enthalpies at the average of the alloy compositions before and after each run.

The temperatures of the liquid alloys for individual runs differed by a maximum of only ±2°K from a mean value of 705°K. The measured values for gold have been corrected for these small differences from 705°K using the value, $\Delta\overline{Cp}_{Au(x_{Sn}=1),\ 700°K} = 3.0$ cal/deg g-atom.[3] Reported heat capacity and heat of mixing data[3] indicate that liquid In-Sn alloys obey Kopp's law. It has thus been assumed that $\Delta\overline{Cp}_{In} = 0$, and the measured values for indium have been directly referred to 705°K.

RESULTS

The experimental values are given in Tables I and II. The data for indium were obtained with respect to liquid indium at 705°K; thus $\Delta\overline{H}_{In} = \overline{H}_{In} - H°_{In(\ell)}$. The data for gold, however, were obtained with respect to solid gold at 705°K. The values of $\Delta\overline{H}_{Au}$ have been referred to supercooled liquid gold at 705°K by assuming the heat of fusion of gold at 705°K to be 2955 cal/g-atom, the same as that at its melting temperature;[3] thus:

$$\Delta\overline{H}_{Au(\ell)} = \overline{H}_{Au} - H°_{Au(\ell)} = \overline{H}_{Au} - H°_{Au(s)} - 2955 \tag{14}$$

The limiting values obtained for the partial molar enthalpies of gold and indium in liquid tin at 705°K are given in Table III. The binary and ternary enthalpy interaction coefficients calculated from the data are summarized in Table IV, which also lists the corresponding values calculated from the random solution model using either Eq. (12) or (13). Limiting binary system data needed for the evaluation of Eq. (12), other than those determined in this study, are listed in the Appendix. Details of the evaluations and interpretations of the values are given in the Discussion.

DISCUSSION

Binary Au-Sn Alloys. The measured partial molar enthalpies of gold are plotted as a function of x_{Au} in Fig. 1. The limiting value of $\Delta\overline{H}_{Au(\ell)}$ at $x_{Sn} = 1$ is obtained as -7955 cal/g-atom (-5000 cal/g-atom with respect to $Au_{(s)}$). The corresponding value from Hultgren et al.[3] is -8010 cal/g-atom, which is based primarily on earlier data from this laboratory. The present data were obtained using samples of both gold and tin of considerably higher purity than those used in any of the previous measurements, and this is believed to be responsible for at least part of the observed difference.

From $x_{Au} = 0$ to ~0.038 the data are represented within a maximum scatter of about ±10 cal/g-atom by the linear relationship:

$$\Delta\overline{H}_{Au(\ell)} = -7955 + 1125x_{Au}, \quad (x_{Au} < 0.038) \qquad (15)$$

where the slope at $x_{Au} = 0$ gives:

$$\eta_{Au}^{Au} = \left(\frac{\partial \Delta\overline{H}_{Au}}{\partial x_{Au}}\right)_{x_{Sn}=1} = 1125 \text{ cal/g-atom}^2 .$$

Thus for $x_{Au} < 0.038$, the enthalpy self-interaction coefficient of gold, η_{Au}^{Au}, remains constant at a value which is only about seven pct of the random solution model value of 15900 cal/g-atom^2. In this composition range, therefore, gold shows only a small departure from Henry's law behavior. This undoubtedly results from the strongly exothermic character of the Au-Sn interaction energy which is indicated by the relatively large negative value of $\Delta\overline{H}_{Au(\ell)}$ at $x_{Au} = 0$. Above $x_{Au} = 0.038$ the departure begins to increase more rapidly, suggesting that the Au-Au interactions begin to become considerably more significant.

From Gibbs-Duhem integration of the values of $\Delta\overline{H}_{Au(\ell)}$, partial molar enthalpies of tin at 705°K have been calculated, yielding the values:

x_{Au}	$\Delta\overline{H}_{Sn}$, cal/g-atom
0.04	-1.0
0.05	-2.3
0.06	-4.8

Thus, as must be expected, the departure of tin from Raoult's law behavior is also small within the measured composition range.

Binary In-Sn Alloys. Measurements of $\Delta\overline{H}_{In}$ in the binary In-Sn system were made only at very dilute compositions (x_{In} = 0.0005-0.0017) at the beginning of the studies on the Ag-In-Sn and Au-In-Sn systems. The average value found, -203 (±10) cal/g-atom at 705° K, is more exothermic than the selected value of Hultgren et al.,[3] -140 cal/g-atom at 773° K, which is based primarily on the data of Kleppa[8] and Cohen et al.[9] at 723° K and 623° K, respectively. More recently, Pool and Lundin[10] reported $\Delta\overline{H}_{In} = -243\,(\pm 30)$ cal/g-atom at 750° K, obtained from measurements of the heat of solution of indium, initially at 273° K, in liquid tin at 750° K, and the enthalpy increment of indium between 273° and 750° K taken from Kelley.[11] The present data were evaluated using enthalpy increment values for indium[3] which incorporate the later Cp data (354°-801° K) of Kaznoff.[12] Recalculation of the data of Pool and Lundin using the latter values[3] yields $\Delta\overline{H}_{In} = -210\,(\pm 30)$ cal/g-atom, in excellent agreement with the present value.

Ternary Ag-Au-Sn Alloys. The partial molar enthalpies of gold in alloys for which $x_{Ag} = 0.039$ are plotted as a function of x_{Au} in Fig. 1. The values are represented within the experimental precision by a curve parallel to that for the binary Au-Sn alloys. The linear range is given by:

$$\Delta\overline{H}_{Au(\ell)} = -8033 + 1125x_{Au}, \ (x_{Au} < 0.038) \qquad (16)$$

where -8033 cal/g-atom is the limiting value at $x_{Au} = 0$ of $\Delta\overline{H}_{Au(\ell)}$ in the ternary system for $x_{Ag} = 0.039$. η^{Au}_{Au} has the same value as in the binary Au-Sn system, 1125 cal/g-atom[2], and again remains constant to $x_{Au} \approx 0.038$.

A few runs were made for alloys in which $x_{Ag} = 0.0199$ and 0.0579. From the data, values of $\Delta\overline{H}_{Au(\ell)}$ at $x_{Au} = 0$ were calculated using the value of η^{Au}_{Au} established by the data in Fig. 1, from the relation:

$$\Delta\overline{H}_{Au,\, x_{Au} = 0} = \Delta\overline{H}_{Au,\, x_{Au}} - 1125x_{Au} \qquad (17)$$

Since for these alloys, $0.0048 < x_{Au} < 0.0125$, the linear relation should apply. The resulting values are plotted vs. x_{Ag} in Fig. 2 together with the values determined from Fig. 1 for $x_{Ag} = 0$ and $x_{Ag} = 0.039$. The curve drawn gives maximum weight to the value at $x_{Ag} = 0.039$, since that is the best established of the ternary values. The slope of this curve at $x_{Ag} = 0$ gives

$$\eta_{Au}^{Ag} = \left(\frac{\partial \Delta \overline{H}_{Au}}{\partial x_{Ag}}\right)_{x_{Sn}=1} = -2000 \text{ cal/g-atom}^2$$

The curve has been drawn assuming η_{Au}^{Ag} to remain constant up to $x_{Ag} \approx 0.04$. A smooth curve could be drawn which would result in a slightly more negative value of η_{Au}^{Ag}, but this is not believed to be justified without more data at the lower compositions.

Because of the observed small departure of gold from Henry's law behavior in these alloys, it is not surprising that the value obtained for η_{Au}^{Ag} does not agree with the calculated random solution value of 2820 cal/g-atom^2. A negative value, which is well established by the data, is not amenable to simple interpretation, however, since the value of η_{Au}^{Au} is not affected by the presence of silver, and since the formation of a Ag-Au bond at the expense of a Au-Sn bond and a Ag-Sn bond should presumably be accompanied by a net endothermic effect. The negative value may result from longer range interactions between Ag and Au atoms which would be expected to make an exothermic contribution.

Ternary Au-In-Sn Alloys. Limiting values of $\Delta\overline{H}_{Au(\ell)}$ at $x_{Au} = 0$, shown plotted vs. x_{In} in Fig. 2, were calculated from the measured values of $\Delta\overline{H}_{Au(\ell)}$ using Eq. (17) for correcting to $x_{Au} = 0$. The concentrations of gold present in the measurements ($x_{Au} = 0.0108 - 0.0159$) were well within the range for which η_{Au}^{Au} was found to remain constant at 1125 cal/g-atom^2 for the Au-Sn and Ag-Au-Sn alloys.

Data for $\Delta\overline{H}_{In}$ as a function of x_{Au} are shown plotted in Fig. 3. It was assumed that for the small concentrations of indium involved in these measurements ($x_{In} = 0.0028 - 0.0133$), the effect of η_{In}^{In} would be undetectable within the experimental precision and could be neglected. (If η_{In}^{In} has the random solution value of 410 cal/g-atom^2, its effect on $\Delta\overline{H}_{In}$ at $x_{In} = 0.01$ would be + 4 cal/g-atom.) To check this assumption two runs were made at a much higher indium content, $x_{In} = 0.051$. The results, plotted in Fig. 3, agree well within the experimental scatter with those obtained at the lower indium contents.

The values of $\Delta\overline{H}_{Au,\, x_{Au}=0}$ vs. x_{In} in Fig. 2 and of $\Delta\overline{H}_{In,\, x_{In}\to 0}$ vs. x_{Au} in Fig. 3 are well represented by straight lines which indicate the values of η_{Au}^{In} and η_{In}^{Au} to remain constant over the measured ranges. The slopes of the lines are identical; thus $\eta_{Au}^{In} = \eta_{In}^{Au} = -4500$ cal/g-atom^2, in accord with the required reciprocity relationship between the two coefficients. This value is about 50 pct more exothermic than that calculated from the random solution model, -3040 cal/g-atom^2. If it is assumed that each gold atom is surrounded by indium and tin atoms only, their ratio being determined by x_{In}/x_{Sn}, the value of η_{Au}^{In} predicted from the binary data is -3245 cal/g-atom^2. The significantly more exothermic value measured thus suggests the existence of a greater than statistical number of Au-In bonds in the dilute ternary alloys. This would be consistent with the highly exothermic interaction between gold and indium indicated by the limiting value of $\Delta\overline{H}_{Au(\ell)}$ in liquid indium, -11200 cal/g-atom, which is over 3000 cal/g-atom more negative than that in liquid tin.

Ternary Ag-In-Sn Alloys. Data for $\Delta\overline{H}_{In}$ as a function of x_{Ag} are shown plotted in Fig. 3. The effect of η_{In}^{In} due to the small concentrations of indium present in the runs (x_{In} = 0.0015 - 0.0115) has been neglected, this assumption again being justified by the results of two runs made at a much higher indium content, x_{In} = 0.051. The data yield the value, η_{In}^{Ag} = -2300 cal/g-atom^2, which appears to remain essentially constant over the measured range ($x_{Ag} < 0.05$), and which is slightly more exothermic than the calculated random solution value, -1870 cal/g-atom^2. That this ternary system more closely approaches random solution behavior is consistent with the relatively small pairwise interaction energies indicated by the limiting $\Delta\overline{H}_i$ values for the respective binary systems. The Ag-Sn and In-Sn interaction energies are small endothermic and exothermic quantities, respectively, and the Ag-In interaction energy is only moderately exothermic.

CONCLUSIONS

Values for the gold-gold, silver-gold, indium-gold, and silver-indium enthalpy interaction coefficients in liquid tin at 705°K appear to be well established by the data, which demonstrates the feasibility of such calorimetric determinations in cases where sufficient precision is obtainable. Values for the Au-In-Sn system are in excellent agreement with the reciprocity requirement that $\eta_{Au}^{In} = \eta_{In}^{Au}$, which provides a good indication of their accuracy.

Comparison of the measured values with those predicted by random solution or Henrian behavior leads to qualitative interpretations in terms of solute atom interactions which appear reasonable. It is interesting to note that, in each case, the measured value of the interaction coefficient differs from that predicted by the random solution assumption by a negative amount. As would be expected, this indicates that the equilibrium configuration has a lower energy than the random one, the decrease in energy more than compensating for the accompanying increase in configurational entropy.

ACKNOWLEDGMENTS

The author is indebted to Prof. Ralph Hultgren, who contributed many pertinent and helpful suggestions, and to Mr. Stanley Ross, who was primarily responsible for execution of the experimental program. The work was performed under the auspices of the U. S. Atomic Energy Commission.

APPENDIX

Limiting Partial Molar Enthalpies in Binary Alloys

(taken from Hultgren et al.[3])

Solvent	i	T, °K	$\Delta\overline{H}_i(x_i=0)$, cal/g-atom
$Ag_{(\ell)}$	$Au_{(\ell)}$	1350	- 4660
$Au_{(\ell)}$	$Ag_{(\ell)}$	1350	- 3860
$In_{(\ell)}$	$Au^{*}_{(\ell)}$	723	-11200
$In_{(\ell)}$	$Ag^{*}_{(\ell)}$	723	- 1200
$Sn_{(\ell)}$	$Ag^{*}_{(\ell)}$	723	870

*Supercooled liquid

REFERENCES

[1] C. Wagner: Thermodynamics of Alloys, pp. 51-53, Addison-Wesley Publishing Co., Reading, Mass., 1962.

[2] C. H. P. Lupis and J. F. Elliott: Trans. Met. Soc. AIME, 1965, vol. 233, pp. 829-30.

[3] R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley: Selected Values of Thermodynamic Properties of Metals and Alloys, John Wiley and Sons, New York, 1963.

[4] E. A. Guggenheim: Mixtures, pp. 29-32, Oxford University Press, London, 1952.

[5] C. B. Alcock and F. D. Richardson: Acta Met., 1958, vol. 6, pp. 385-95.

[6] R. L. Orr, A. Goldberg, and R. Hultgren: Rev. Sci. Instr., 1957, vol. 28, pp. 767-73.

[7] R. Hultgren, R. L. Orr, and K. K. Kelley: Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys, (current loose-leaf sheets), Inorganic Materials Research Division, Lawrence Radiation Laboratory, University of California, Berkeley, California, 1964-present.

[8] O. J. Kleppa, J. Phys. Chem., 1956, vol. 60, pp. 842-46.

[9] J. P. Cohen, B. W. Howlett, and M. B. Bever: Trans. Met. Soc. AIME, 1961, vol. 221, pp. 683-86.

[10] M. J. Pool and C. E. Lundin: *Trans. Met. Soc. AIME*, 1964, vol. 230, pp. 589-91.

[11] K. K. Kelley: *U.S. Bur. Mines Bull. no. 584*, 1960.

[12] A. I. Kaznoff: *Thermal Properties of Indium*, Ph. D. Thesis, University of California, Berkeley, California, 1961.

Table I. Experimental Data: $\Delta\overline{H}_{Au(\ell)}$ in Au-Sn, Ag-Au-Sn, and Au-In-Sn Alloys at 705° K

Au-Sn Alloys		Ag-Au-Sn Alloys			Au-In-Sn Alloys		
x_{Au} (avg)	$\Delta\overline{H}_{Au(\ell)}$ cal/g-at	x_{Ag} (avg)	x_{Au} (avg)	$\Delta\overline{H}_{Au(\ell)}$ cal/g-at	x_{In} (avg)	x_{Au} (avg)	$\Delta\overline{H}_{Au(\ell)}$ cal/g-at
0.00035	-7964	0.0199	0.0048	-8010	0.0045	0.0108	-7965
0.00070	-7971	"	0.0062	-7985	"	0.0122	-7970
0.00074	-7943	0.0390	0.0007	-8016	0.0100	0.0036	-8000
0.0011	-7955	"	0.0021	-8047	"	0.0051	-8012
0.0018	-7951	"	0.0034	-8026	0.0200	0.0065	-8044
0.0021	-7942	"	0.0048	-8045	"	0.0079	-8034
0.0022	-7958	"	0.0074	-8012	0.0311	0.0092	-8094
0.0028	-7963	"	0.0088	-7999	"	0.0106	-8097
0.0035	-7962	"	0.0116	-8018	0.0408	0.0119	-8129
0.0042	-7945	"	0.0129	-8024	"	0.0133	-8124
0.0056	-7940	"	0.0236	-8006	0.0495	0.0145	-8159
0.0069	-7946	"	0.0248	-7990	"	0.0159	-8170
0.0083	-7944	"	0.0339	-8013			
0.0197	-7936	"	0.0351	-7991			
0.0210	-7929	"	0.0452	-7977			
0.0308	-7928	"	0.0464	-7968			
0.0320	-7909	"	0.0556	-7929			
0.0410	-7902	"	0.0568	-7943			
0.0422	-7913	0.0597	0.0099	-8052			
0.0510	-7871	"	0.0112	-8015			
0.0522	-7875	"	0.0125	-8019			
0.0582	-7843						
0.0594	-7845						

Table II. Experimental Data: $\Delta\overline{H}_{In}$ in In-Sn, Au-In-Sn, and Ag-In-Sn Alloys at 705° K

Au-In-Sn Alloys

x_{Au} (avg)	x_{In} (avg)	$\Delta\overline{H}_{In}$ cal/g-at
0	0.00056	-205
0	0.0017	-210
0.0058	0.0105	-224
"	0.0116	-226
0.0101	0.0028	-260
"	0.0039	-265
0.0166	0.0500*	-270
"	0.0511*	-273
0.0193	0.0051	-283
"	0.0063	-269
0.0277	0.0074	-340
"	0.0085	-326
0.0398	0.0096	-379
"	0.0109	-384
0.0498	0.0120	-422
"	0.0133	-427

Ag-In-Sn Alloys

x_{Ag} (avg)	x_{In} (avg)	$\Delta\overline{H}_{In}$ cal/g-at
0	0.00047	-195
0.0100	0.0015	-238
"	0.0026	-226
0.0198	0.0037	-242
"	0.0048	-254
0.0295	0.0060	-248
"	0.0071	-274
0.0390	0.0082	-291
"	0.0094	-298
0.0464	0.0503*	-296
"	0.0515*	-298
0.0484	0.0104	-327
"	0.0115	-308

---

*Runs made at higher x_{In} to check for effect of η_{In}^{In}.

Table III. Measured Limiting Partial Molar Enthalpies in Liquid Tin at 705°K

Solute (i)	$\Delta\overline{H}_{i(\ell)}, x_{Sn}=1$ cal/g-atom	$\Delta\overline{H}_{i(s)}, x_{Sn}=1$ cal/g-atom
Au	-7955 (±15)	-5000 (±15)
In	-203 (±10)	—

Table IV. Enthalpy Interaction Coefficients in Liquid Tin-Rich Alloys at 705°K

Interaction Coefficient	Measured Value cal/g-atom^2	Random Sol'n Value cal/g-atom^2
η_{Au}^{Au}	1125	15900
η_{In}^{In}	—	410
η_{Au}^{Ag}	-2000	2820
η_{Au}^{In}	-4500	-3040
η_{In}^{Au}	-4500	-3040
η_{In}^{Ag}	-2300	-1870

List of Figures

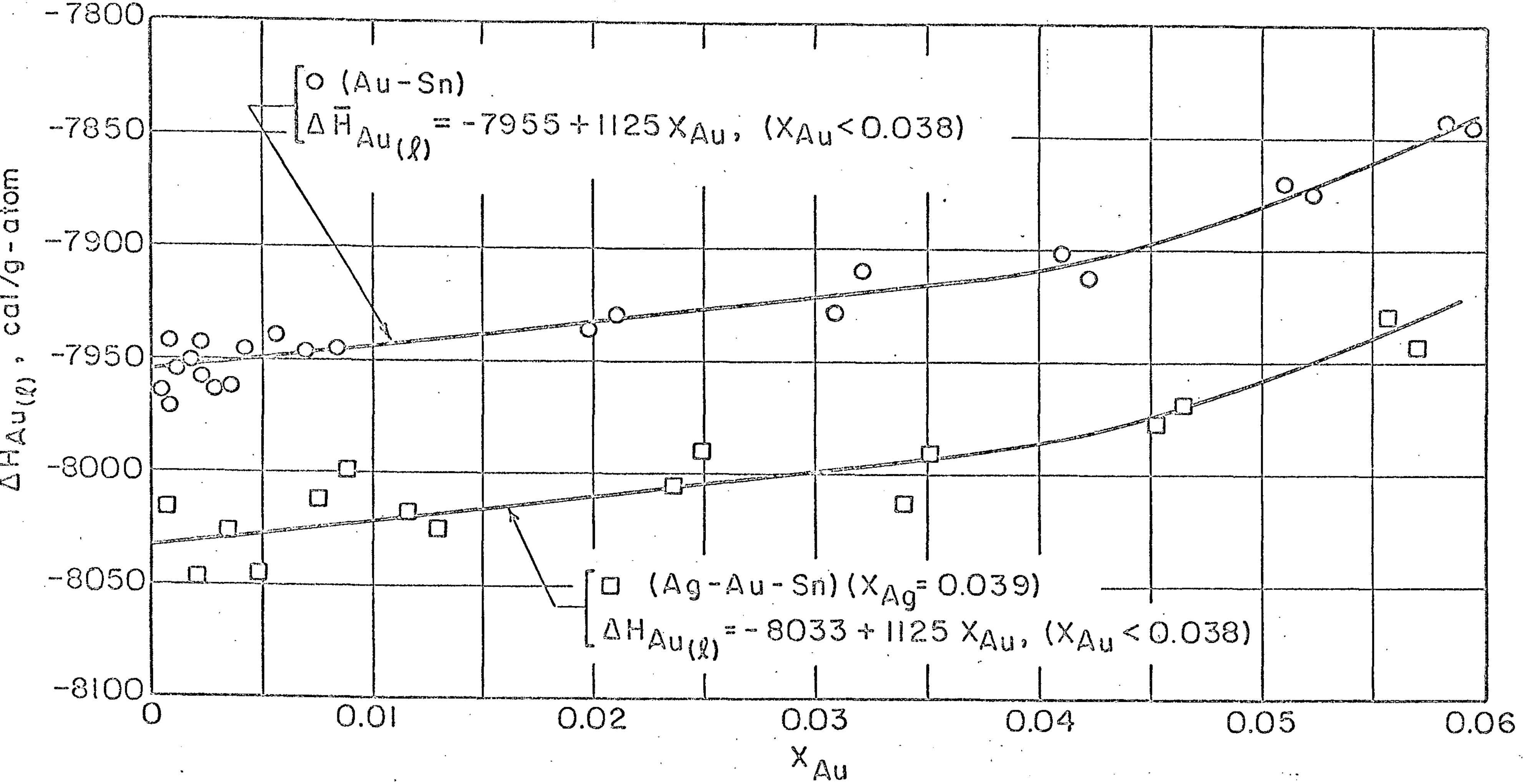

FIG. 1 DATA FOR PARTIAL MOLAR ENTHALPY OF GOLD IN LIQUID (Au-Sn) AND (Ag-Au-Sn)$_{(X_{Ag}=0.039)}$ ALLOYS AT 705°K.

MUB-9527

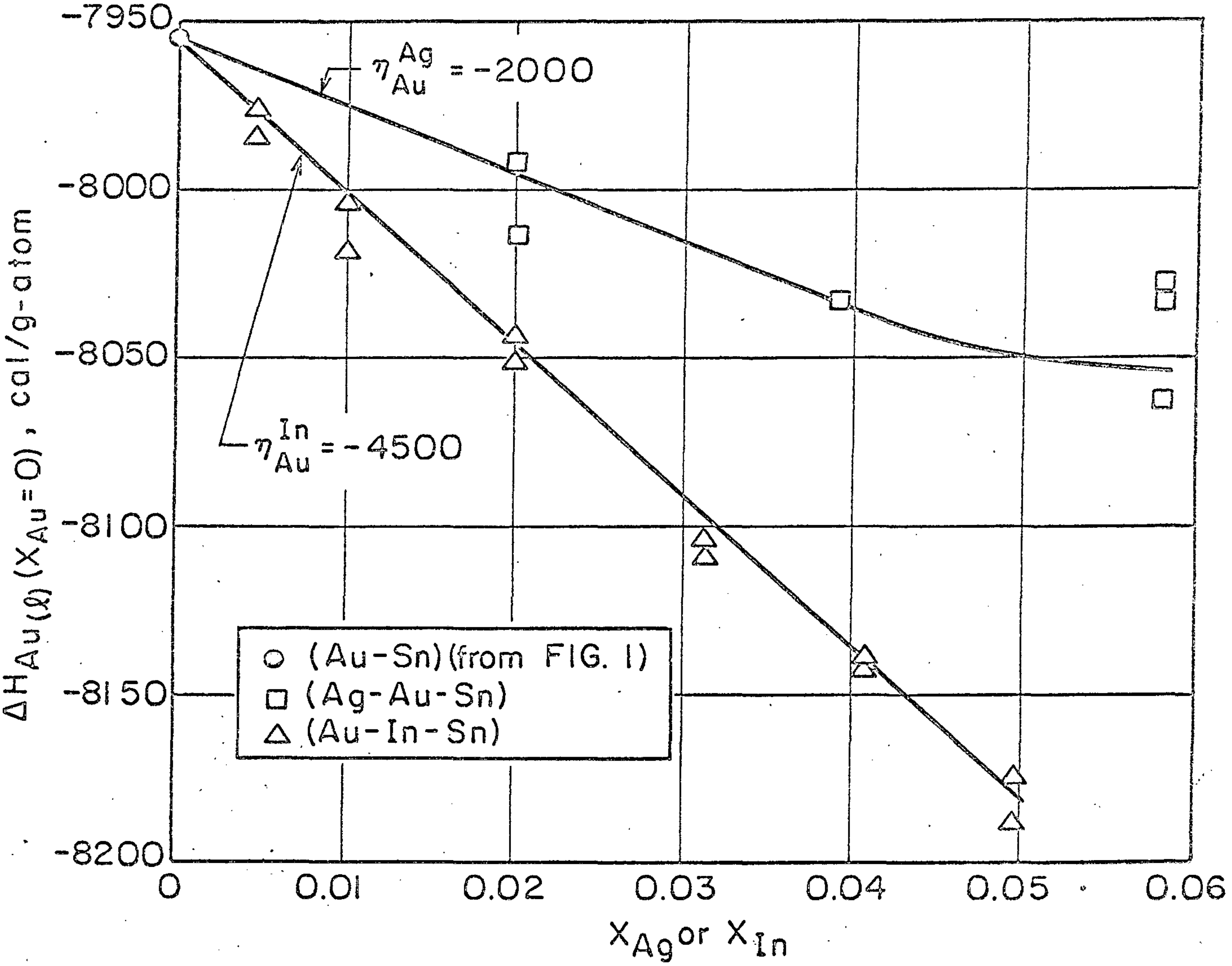

FIG. 2. EFFECT OF SILVER AND INDIUM ON THE PARTIAL MOLAR ENTHALPY OF GOLD ($X_{Au}=0$) IN LIQUID TIN-RICH ALLOYS AT 705°K.

MUB-9528

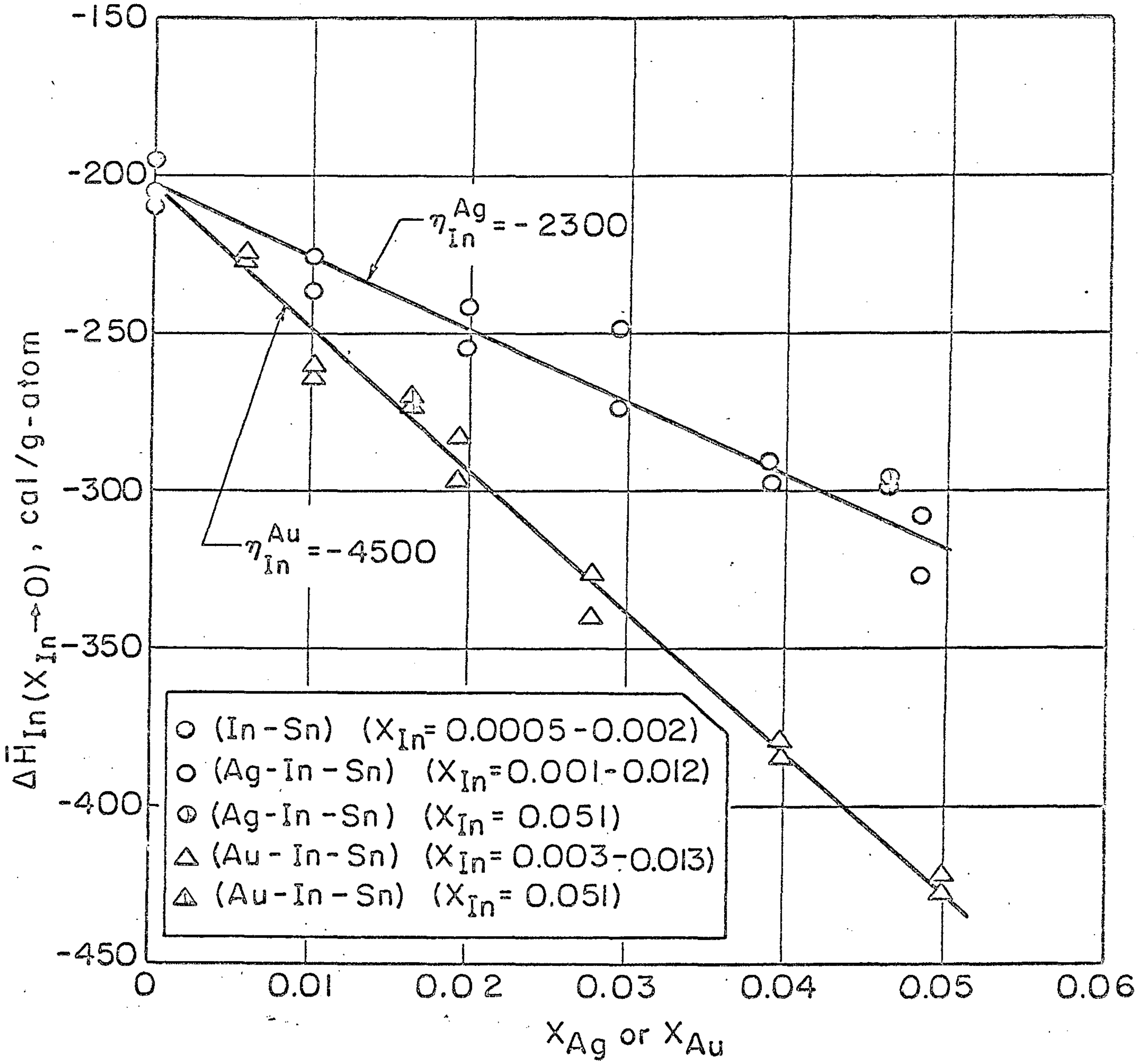

FIG. 3 EFFECT OF SILVER AND GOLD ON THE PARTIAL MOLAR ENTHALPY OF INDIUM ($X_{In}\to 0$) IN LIQUID TIN-RICH ALLOYS AT 705°K.

MUB-9529