N68-33665

THERMODYNAMIC ANALYSIS OF DILUTE TERNARY SYSTEMS - I. THE AG-AU-SN SYSTEM

P. J. Spencer, et al

Denver University
Denver, Colorado

DISTRIBUTED BY: CLEARINGHOUSE
FOR FEDERAL SCIENTIFIC AND TECHNICAL INFORMATION

U. S. DEPARTMENT OF COMMERCE / NATIONAL BUREAU OF STANDARDS

FACILITY FORM 602

[illegible]
(ACCESSION NUMBER)

21
(PAGES)

CR 87774
(NASA CR OR TMX OR AD NUMBER)

(CODE)

33
(CATEGORY)

THERMODYNAMIC ANALYSIS OF DILUTE TERNARY SYSTEMS

I. The Ag-Au-Sn System

P. J. Spencer and M. J. Pool*

ABSTRACT

The heats of solution of silver and gold in dilute Ag-Au-Sn alloys have been determined as a function of alloy composition using liquid metal solution calorimetry. From the values obtained, the various enthalpy interaction parameters in the liquid solutions have been calculated. The results are interpreted in terms of the probable bonding changes taking place between silver, gold and tin atoms.

INTRODUCTION

Addition of a second solute to a dilute binary alloy may cause striking changes in the thermodynamic characteristics of the alloy. As yet, such influences cannot be reliably predicted and it is only by accumulation and critical assessment of data that definite patterns can be established.

Solute interactions in dilute solutions were first treated mathematically by Wagner$^{(1)}$, who derived expressions for the Gibbs energy interaction coefficients. For an alloy consisting of two dilute solutes, i and j, in a solvent s, these coefficients are given by:

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

---

*P. J. Spencer and M. J. Pool, Junior Member AIME, are Research Associate and Associate Professor, Department of Metallurgy, University of Denver, Denver, Colorado

[redacted]

CFSTI
H.C 3.00
Cat 33

where γ_i is the activity coefficient of component i and x represents the mole fraction of solute or solvent.

Other interaction coefficients have since been established in terms of the various partial molar thermodynamic properties of an alloy; the definitions of these are summarized in a recent paper by Lupis and Elliott.(2)

Mathematical and experimental studies of such coefficients have received much attention recently,(2-7) providing a very useful theoretical background to an understanding of the nature of solute interactions taking place in dilute solutions. One of the definitions to arise from such work has been the extension of Wagner's treatment by Lupis and Elliott(4) to include an enthalpy interaction coefficient, defined as:

$$\eta_i^j = \left(\frac{\partial \overline{\Delta H}_i}{\partial x_j}\right)_{x_s=1} \qquad (2)$$

where $\overline{\Delta H}_i$ is the relative partial molar enthalpy of component i.

$\overline{\Delta H}_i$ is related to the relative partial molar enthalpy at infinite dilution, $\overline{\Delta H}_i^\circ$, and to the enthalpy interaction coefficients by the expression:

$$\overline{\Delta H}_i = \overline{\Delta H}_i^\circ + x_i\eta_i^i + x_j\eta_i^j + \ldots \qquad (3)$$

Values of $\overline{\Delta H}_i$ can often be determined with a high degree of accuracy by calorimetry and equation (2) thus enables reliable enthalpy interaction coefficients to be calculated. Partial heats of solution must be investigated as a function of solute concentrations down to $x_i=0$ and since η values are obtained from the slope of $\overline{\Delta H}_i$ plotted against x, great care must be taken to obtain precise data. The data for binary systems which are presently available often require extrapolation of $\overline{\Delta H}_i$ values from compositions as great as $x_i = 0.05$ or even 0.1 to obtain limiting heats of solution: Reliable enthalpy interaction coefficients are thus impossible to obtain for most of the alloy systems already investigated.

The aim of the present work was to determine values of q for the relatively simple Ag-Au-Sn system and from these results to gain some insight into the possible influence of a second solute upon the alloying characteristics of a dilute binary alloy. It was hoped to express observed behavior in terms of bonding changes taking place between the component atoms of the alloy.

EXPERIMENTAL

The liquid metal solution calorimeter used in this research has been described elsewhere(8) and only a very brief outline of its construction and operation will therefore be given here.

The calorimeter consists essentially of a liquid tin or alloy bath used as the solvent and maintained at a constant temperature, to within ± 1/4°C, inside an evacuated isothermal jacket. The solution of a specimen in the bath is accompanied either by liberation or absorption of heat and the resulting temperature change is detected by a multi-junction thermopile surrounding the bath. The output from this is connected differentially with that from an identical thermopile which surrounds a 'passive' calorimeter well under identical environmental conditions. The resulting e.m.f. is amplified and fed into a chart recorder; the temperature change accompanying the solution process is thus automatically recorded in graphical form. The method of obtaining heat of solution values from such a plot has been described frequently and needs no further discussion here.

For each series of experimental drops, a solvent bath consisting of approximately 80 gms of 99.99% pure tin was carefully weighed and inserted in the calorimeter. The appropriate amount of either 99.999% pure Au or Ag (supplied by A. D. Mackay Inc.) was then added in order to obtain an alloy of the desired composition. The bath was stirred continuously throughout the experiments in order to ensure complete homogeneity of the alloys. When the heat of solution of Au in the bath was being investigated, specimens equivalent to about .0025 mole were weighed out; for Ag approximately .00125 mole additions were used. The calorimeter heat capacity was determined throughout using tin or tungsten calibration samples.

The heats of solution of Au and Ag in pure tin were first determined separately as a function of their concentration in order to obtain the self-interaction parameters η_{Au}^{Au} and η_{Ag}^{Ag}. Alloys containing between 0 and 0.04 mole fraction of either Ag or Au were then used as the solvent bath and values of either $\overline{\Delta H}_{Au(\ell)}$ or $\overline{\Delta H}_{Ag(\ell)}$ were obtained as before. The composition of the bath was kept constant at the desired Au or Ag concentration (to within ± .0003 mole fraction) by making calculated additions of the appropriate solute throughout the experiment. Heat of solution values were calculated using the heat content data of Hultgren et al.(9) and a correction for the heat of fusion of Au or Ag at the experimental temperature was made.

RESULTS AND DISCUSSION

Binary Au-Sn Alloys

Experimental values for the heat of solution of gold in liquid tin as a function of gold concentration are given in Table 1 and are plotted graphically in Figure 1. The value of $\overline{\Delta H}^{\circ}_{Au(\ell)}$ at 723°K is obtained as -8075 cal/g-atom, which is somewhat more exothermic than the value of -7970 cal/g.-atom given by

Hultgren's standard data. Between 0 and 0.05 mole fraction Au the variation of the heat of solution with increasing gold concentration was found by a least squares analysis to follow the linear relation:

$$\overline{\Delta H}_{Au(l)} = -8075 + 2413\, x_{Au} \qquad (4)$$

Experimental points deviate on the average by less than ± 25 cals/g.-atom from the straight line.

The self interaction parameter, $\eta_{Au}^{Au} = \left(\frac{\partial\, \overline{\Delta H}_{Au}}{\partial\, x_{Au}}\right)_{(x_{Sn}=1)}$, is thus obtained as 2413 cal./g.-atom and this can be compared with the value of 1125 cal./g.-atom at 703°K, determined by Orr.(10) η_{Au}^{Au} thus appears to become more positive with increasing temperature. Recent work by Jena and Leach(11) between 548°K and 723°K also confirms this trend, but since their investigation was concerned with the entire composition range of the Au-Sn system, no measurements were made of $\overline{\Delta H}_{Au}$ for alloys between $x_{Au}=0$ and $x_{Au}=0.1$. Thus, the exact slope of $\overline{\Delta H}_{Au(l)}$ vs x_{Au} cannot be accurately obtained from their data.

The random solution model predicts a value of η_{Au}^{Au} which is given by $-2\overline{\Delta H}^{\circ}_{Au(l)}$ and using the results obtained in the present work this yields a self-interaction parameter of 16,150 cal./g.-atom. The experimental value is thus very much less than the theoretical, although the observed general trend of an increase in η_{Au}^{Au} with temperature would be expected if the reasonable assumption is made that the liquid alloy more closely approximates a random solution with increase in temperature.

The results show that η_{Au}^{Au} remains constant up to about 0.05 mole fraction Au, after which $\overline{\Delta H}_{Au(\ell)}$ becomes increasingly more endothermic. It would seem that beyond this composition, the initial strong attraction between gold and tin atoms (shown by the relatively large limiting heat of solution) is tempered somewhat by an increase in Au-Au atomic interactions.

Binary Ag-Sn Alloys

The data obtained for these alloys are listed in Table 1 and illustrated in Figure 2. The heat of solution of silver in liquid tin is endothermic and a value of $\overline{\Delta H}^{\circ}_{Ag(\ell)}$ of 967 cal./g.-atom was obtained. Between $x_{Ag}=0$ and 0.035, the results can be represented by the linear equation:

$$\overline{\Delta H}_{Ag(\ell)} = 967-6322\ x_{Ag} \qquad (5)$$

The average deviation of experimental points from the straight line is ± 34 cals./g.-atom.

The present data show excellent agreement with previous work by Pool(8) and by Oriani and Murphy(12) both in the limiting value of the heat of solution and in the composition dependence of $\overline{\Delta H}_{Ag(\ell)}$. The experimental value of η_{Ag}^{Ag} at 723°K is -6322 cal./g.-atom, while the random solution model, when combined with the present data, predicts a figure of -1934 cal./g.-atom.

The present results are plotted in Figure 3, together with those of Pool(8) at 655°K, 700°K and 750°K and of Oriani and Murphy(12) at 723°K. The data illustrate the variation of η_{Ag}^{Ag} with temperature and compare these data with the predictions of the random solution model. It can be seen that, as in the case of the Au-Sn alloys, the higher the temperature the more closely does the value of the self-interaction parameter approach random solution behavior. It should be pointed out, however, that the values of η_{Ag}^{Ag} as given by Oriani and Murphy's data at 579°K and 915°K result in greater divergence of their results from random solution behavior with increasing temperature. Such a trend is somewhat surprising.

The endothermic value for $\overline{\Delta H}^{\circ}_{Ag(\ell)}$ suggests that there is some repulsion between silver and tin atoms on introduction of the solute, but the repulsive Ag-Sn forces are reduced as the silver concentration increases.

Ternary Ag-Au-Sn Alloys

Subsequent to investigations of the dilute binary alloys discussed above, further measurements were made at 723°K of $\overline{\Delta H}_{Au(\ell)}$ in Ag-Au-Sn alloys of constant silver concentration and of $\overline{\Delta H}_{Ag(\ell)}$ in ternary alloys of constant gold concentration. The results are summarized in Table 2. Particular attention was given to alloys containing 0.04 mole fraction Au or Ag respectively so that the values of η_{Au}^{Ag} and η_{Ag}^{Au} might be well-established over the range from 0 to 0.04 mole fraction where no deviation from linearity of the $\overline{\Delta H}$ values was anticipated. Further, a direct comparison with the equivalent data of Orr at 703°K could then be made.

It was found that the heat of solution of gold in a 0.04 mole fraction Ag-Sn alloy could be expressed by the relationship:

$$\overline{\Delta H}_{Au(\ell)} = -8181 + 2443\, x_{Au} \quad \text{(0 to 0.05 mole fraction Au)} \qquad (6)$$

The average deviation of experimental points from the straight line is ± 16 cals/mole.

The data are plotted in Figure 1 where it can be seen that the limiting heat of solution is slightly more exothermic than in binary Au-Sn alloys, although the value of η_{Au}^{Au} at 2443 cal/g-atom is identical to the binary result within the experimental limits. This behavior agrees well with Orr's observations at the lower temperature. The presence of silver atoms in the liquid alloys thus appears to have very little influence on the nature of the atomic interactions in the gold-tin system apart from causing a small increase in heat of solution values.

$\overline{\Delta H}_{Au(\ell)}$ was also determined in alloys containing 0.01, 0.02 and 0.03 mole fraction Ag, but fewer gold drops were made at these intermediate silver concentrations since η_{Au}^{Au} had already been found to have the same value in both 0 and 0.04 mole fraction Ag alloys. While $\overline{\Delta H}^{\circ}_{Au(\ell)}$ is therefore not so accurately established, it can be seen from Figure 4 that the few drops which were made in each case nevertheless permitted calculation of limiting heat of solution values which lie on a good straight line plot between 0 and 0.04 mole fraction Ag. The slope of this line gives a value for η_{Au}^{Ag} of -2650 cal/g.-atom at 723°K compared with Orr's value of -2000 cal/g.-atom at 703°K. The theoretical value for η_{Au}^{Ag} based on a modified quasi-chemical solution model$^{(13)}$ and using the present data is 2448 cal/g.-atom, so that the experimental results and solution model theory differ in sign.

Values for the heat of solution of silver in a 0.04 mole fraction Au-Sn alloy again show a linear dependence of $\overline{\Delta H}_{Ag}$ with composition between 0 and 0.035 mole fraction Ag as shown in Figure 5. A least squares treatment gives the expression:

$$\overline{\Delta H}_{Ag(\ell)} = 964 - 8883\ x_{Ag} \qquad (7)$$

The average deviation of experimental points from the straight line is ± 32 cals/g.-atom.

The limiting heat of solution of silver is thus almost identical to that obtained for the binary Ag-Sn alloys, but the slope of $\overline{\Delta H}_{Ag}$ vs x_{Ag} is steeper in this case, giving a value of -8883 cal/g.-atom for η^{Ag}_{Ag}. The presence of Au atoms in the solution results in more exothermic values of $\overline{\Delta H}_{Ag}$ at given Ag concentrations than those observed in binary silver-tin alloys. This would be expected from the exothermic nature of Au-Ag interactions.$^{(9)}$ Since $\overline{\Delta H}^{\circ}_{Ag(\ell)}$ in the binary Ag-Sn and ternary 0.04 mole fraction Au-Ag-Sn alloys has the same value, η^{Au}_{Ag} is obtained as zero within experimental limits. From the Maxwell-type relationships which can be applied to partial molar properties it is found that η^{Ag}_{Au} should be equal to η^{Au}_{Ag}. The present experimental data do not therefore conform to the predictions of theory. Measurements were made of $\overline{\Delta H}_{Ag(\ell)}$ in a 0.02 mole fraction Au-Sn alloy in an attempt to confirm the constancy of its limiting value in the binary and ternary alloys. While fewer silver drops were made in this case and $\overline{\Delta H}^{\circ}_{Ag(\ell)}$ must be regarded as somewhat less accurate, its value at approximately 940 cals/g.-atom still lies within experimental limits from the other two limiting values.

CONCLUSIONS

The present results indicate two different ways in which a second solute can affect the thermodynamic characteristics of a dilute binary alloy.

a) The presence of 0.04 mole fraction Ag in dilute Au-Sn alloys results in more exothermic values of $\overline{\Delta H}_{Au(\ell)}$ at given Au concentrations but does not change the self-interaction parameter, η^{Au}_{Au}.

b) The presence of 0.04 mole fraction Au in dilute Ag-Sn alloys changes the self-interaction parameter η_{Ag}^{Ag} but does not change the limiting heat of solution, $\overline{\Delta H}^{\circ}_{Ag(\ell)}$.

When the present data are combined with results obtained by other workers at different temperatures, it is found that dilute binary Au-Sn and Ag-Sn alloys tend to approach theoretical random solution behavior with increase in temperature.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the financial support of the National Aeronautics and Space Administration Research Grant No. NsG-518. Acknowledgement is also given to Dr. C. B. Magee of the University of Denver for discussion of the manuscript.

REFERENCES

1. C. Wagner; Thermodynamics of Alloys, Addison-Wesley Publishing Co. Reading, Mass., 1952
2. C. H. P. Lupis and J. F. Elliott; Acta Met. 1966, 14, 529
3. J. M. Dealy and R. D. Pehlke; Trans. Met. Soc. A.I.M.E., 1963, 227, 88.
4. C. H. P. Lupis and J. F. Elliott; Trans. Met. Soc. A.I.M.E., 1965, 233, 829.
5. J. V. Gluck and R. D. Pehlke; Trans. Met. Soc. A.I.M.E., 1967, 239, 36
6. L. S. Darken; Trans. Met. Soc. A.I.M.E., 1967, 239, 90
7. C. H. P. Lupis and J. F. Elliott; Acta Met., 1967, 15, 265.
8. M. J. Pool; Trans. Met. Soc. A.I.M.E., 1965, 233, 1711.
9. 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.
10. R. L. Orr; Trans. Met. Soc. A.I.M.E., 1966, 236, 1445.
11. A. K. Jena and J. S. Ll. Leach; Acta Met., 1966, 14, 1595.
12. R. A. Oriani and W. K. Murphy; Acta Met., 1962, 9, 879.
13. C. B. Alcock and F. D. Richardson; Acta Met., 1958, 6, 385.

LIST OF TABLES

TABLE 1.

Partial Heats of Solution of Au and Ag in Au-Sn and Ag-Sn Alloys at 723°K

Binary Au-Sn Alloys

X_{Au} avg.	$\overline{\Delta H}_{Au}(\ell)$ cal./g-atom
.0024	-8099
.0046	-8060
.0113	-8050
.0156	-8017
.0188	-8069
.0222	-7969
.0255	-8029
.0289	-8021
.0326	-7972
.0364	-7954
.0403	-7925
.0439	-8031
.0480	-7977
.0520	-7959
.0583	-7891
.0622	-7891
.0660	-7855
.0691	-7860

Binary Ag-Sn Alloys

X_{Ag} avg.	$\overline{\Delta H}_{Ag}(\ell)$ cal./g-atom
.0012	980
.0034	925
.0053	880
.0071	967
.0107	915
.0126	905
.0161	871
.0181	804
.0215	911
.0233	771
.0254	799
.0272	861
.0287	753
.0345	808
.0364	640
.0384	643
.0400	633
.0418	587
.0437	742
.0454	700
.0473	587
.0491	466
.0505	599
.0519	442
.0533	441
.0549	441
.0565	405

TABLE 2.

Partial Heats of Solution of Au and Ag in Ag-Au-Sn Alloys at 723°K

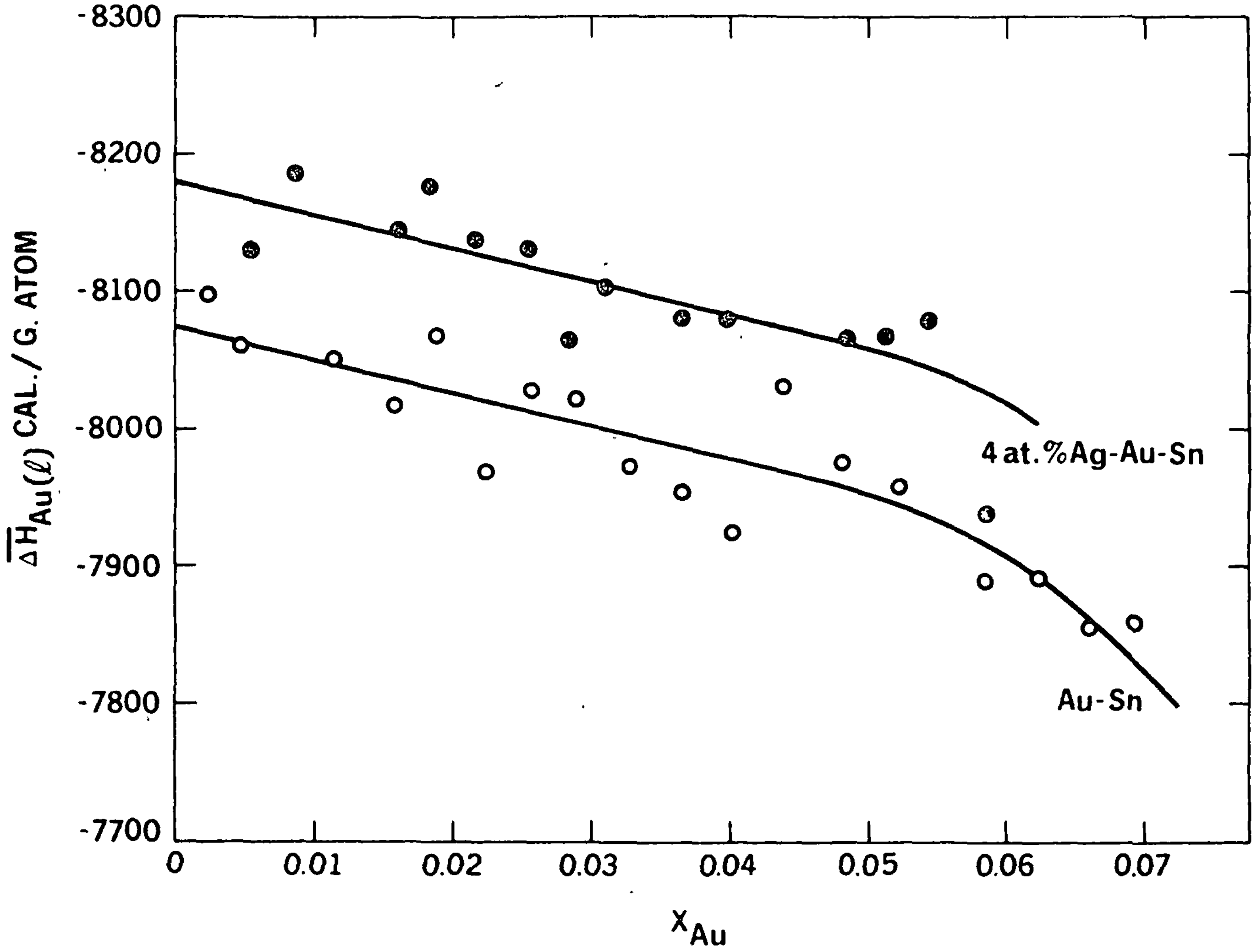
Ternary Ag-Au-Sn Alloys

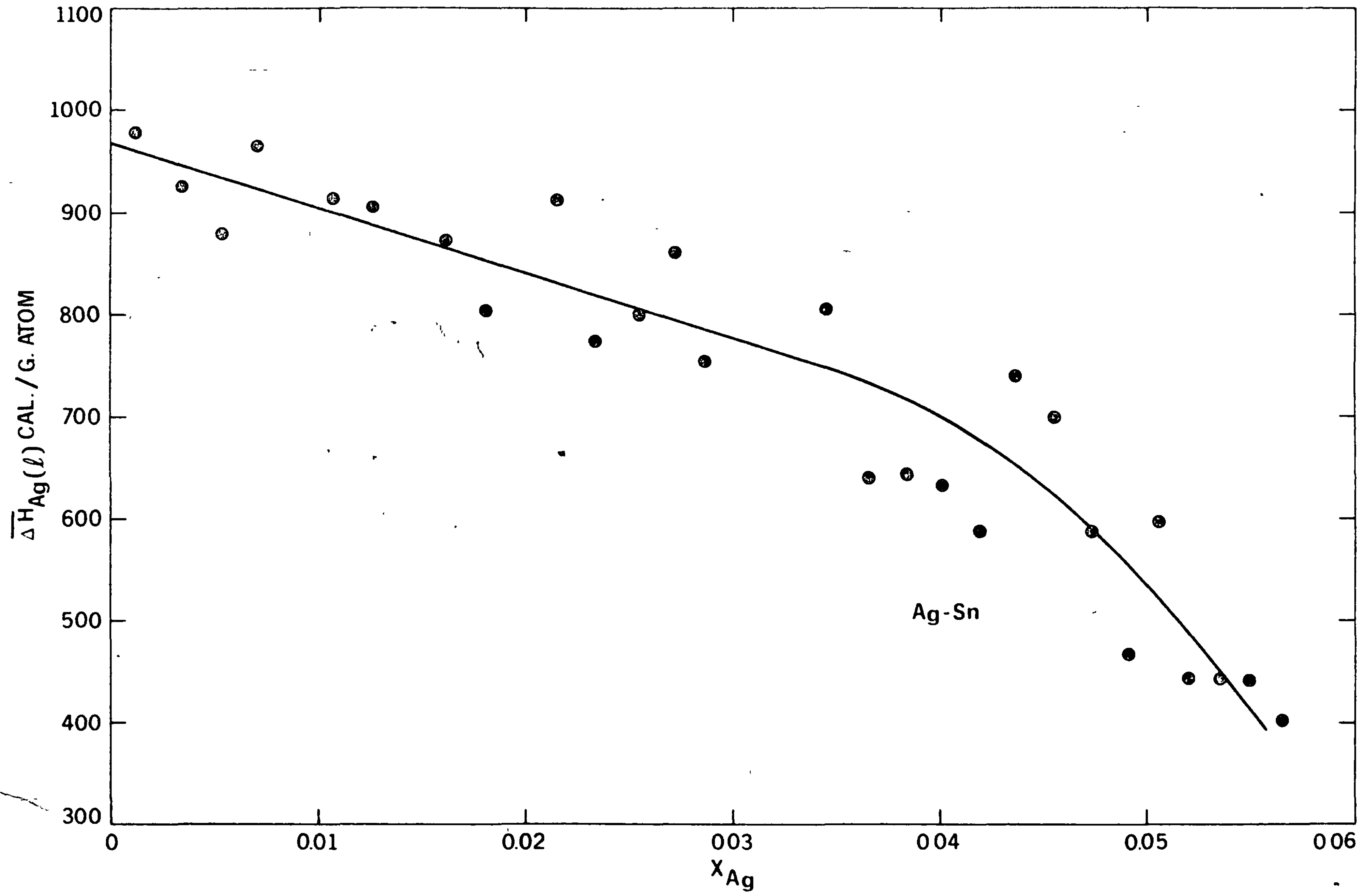
x_{Ag} avg.	x_{Au} avg.	$\overline{\Delta H}_{Au(\ell)}$ cal./g-atom
.0099	.0018	-8188
.0099	.0052	-8144
.0099	.0086	-8106
.0099	.0123	-8100
.0099	.0158	-8012
.0099	.0189	-8146
.0200	.0018	-8094
.0200	.0052	-8134
.0300	.0018	-8133
.0300	.0018	-8162
.0300	.0050	-8161
.0300	.0053	-8135
.0300	.0088	-8118
.0300	.0088	-8100
.0399	.0053	-8131
.0399	.0087	-8186
.0399	.0159	-8144
.0399	.0182	-8177
.0399	.0216	-8139
.0399	.0253	-8132
.0399	.0283	-8065
.0399	.0308	-8103
.0399	.0365	-8081
.0399	.0397	-8079
.0399	.0484	-8067
.0399	.0511	-8068
.0399	.0544	-8080
.0399	.0585	-7938

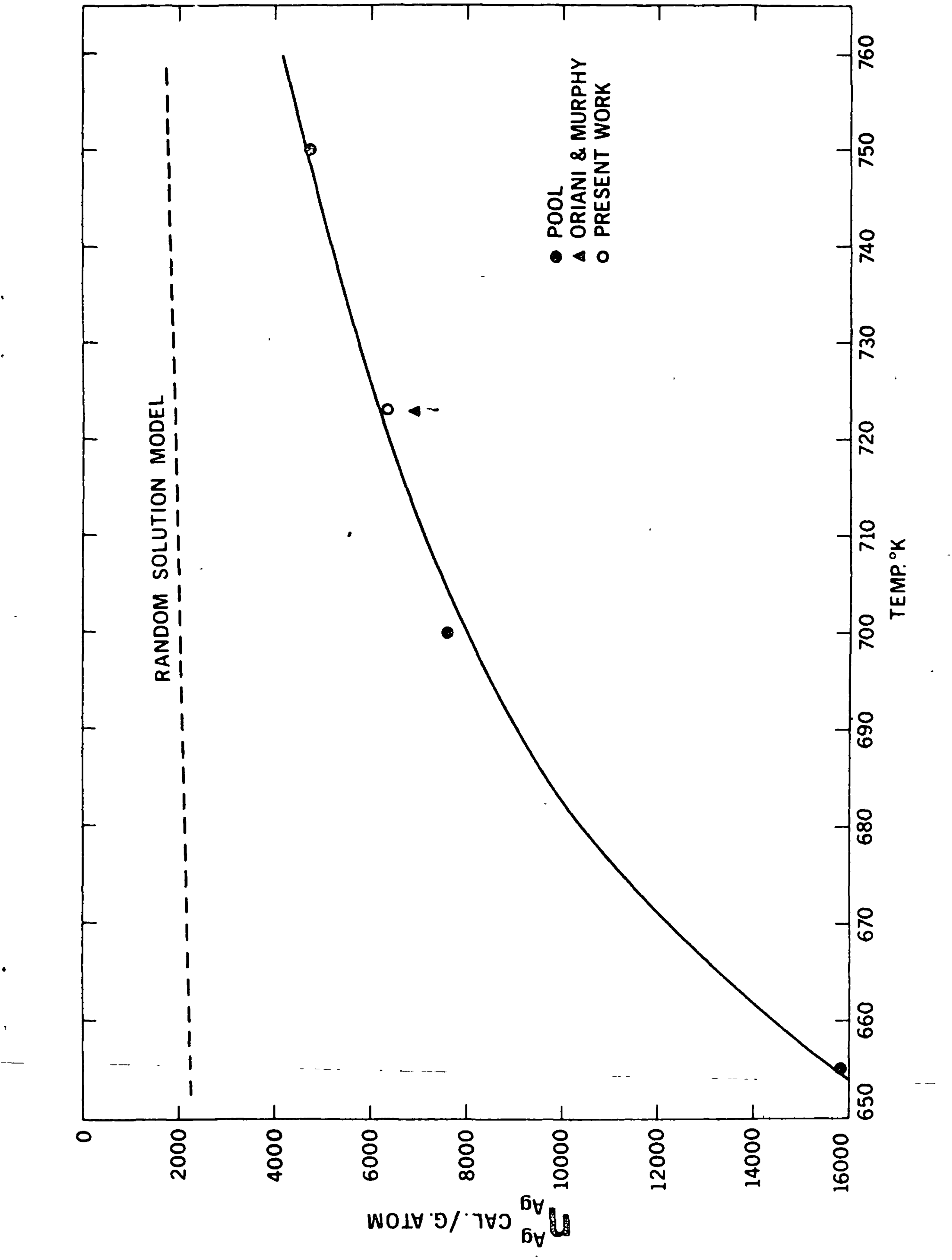
Ternary Ag-Au-Sn Alloys

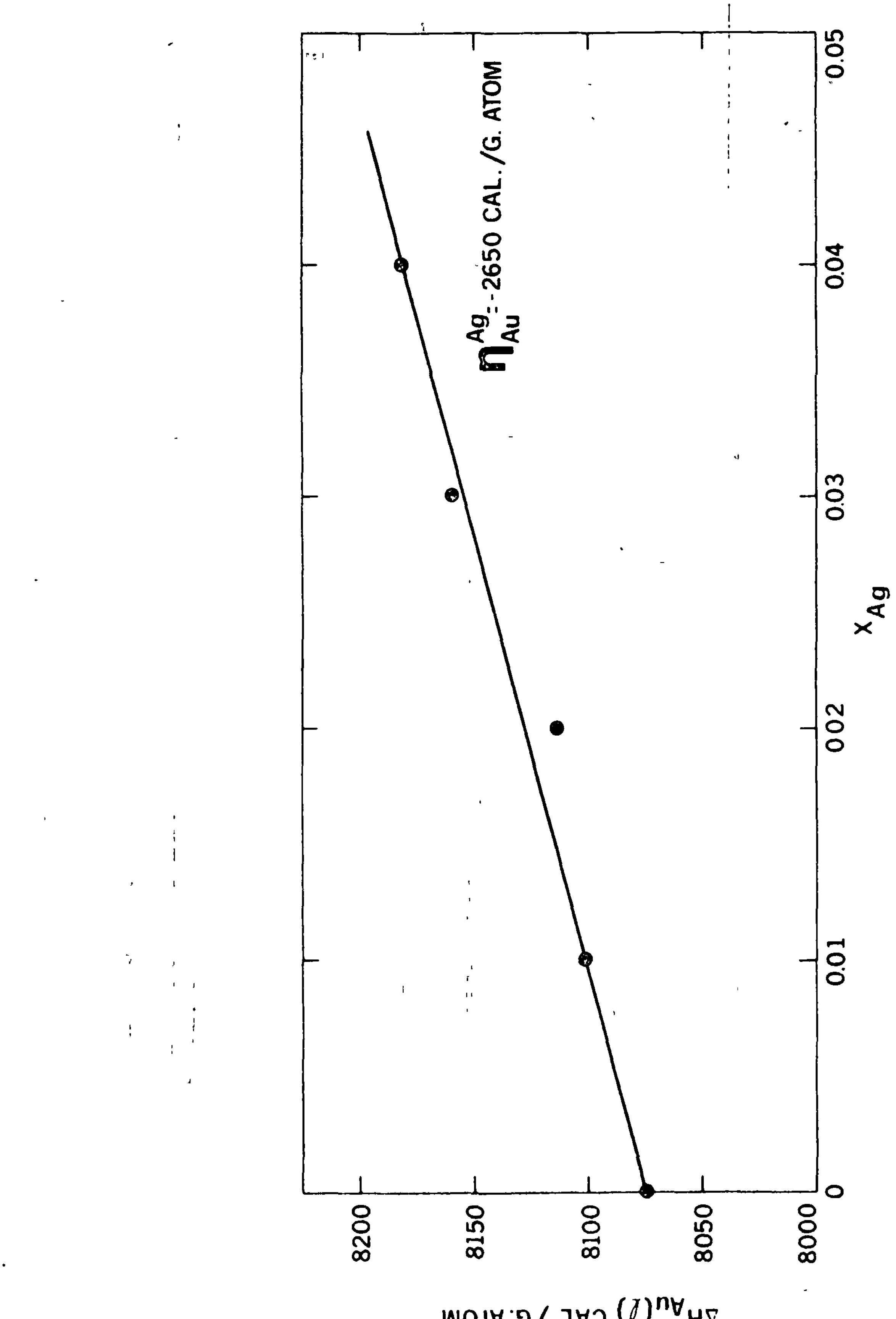
x_{Au} avg.	x_{Ag} avg.	$\overline{\Delta H}_{Ag(\ell)}$ cal./g-atom
.0199	.0009	983
.0199	.0026	815
.0199	.0044	944
.0199	.0063	871
.0199	.0081	731
.0399	.0009	940
.0399	.0027	950
.0399	.0031	945
.0399	.0052	877
.0399	.0071	987
.0399	.0072	836
.0399	.0092	835
.0399	.0104	913
.0399	.0012	902
.0399	.0018	865
.0399	.0151	843
.0399	.0167	819
.0399	.0197	733
.0399	.0227	720
.0399	.0243	786
.0399	.0258	808
.0399	.0274	706
.0399	.0291	697
.0399	.0308	723
.0399	.0323	669
.0399	.0339	600
.0399	.0356	669
.0399	.0373	659
.0399	.0391	556
.0399	.0407	574
.0399	.0422	562
.0399	.0439	541
.0399	.0458	482
.0399	.0476	495
.0399	.0491	393
.0399	.0507	406

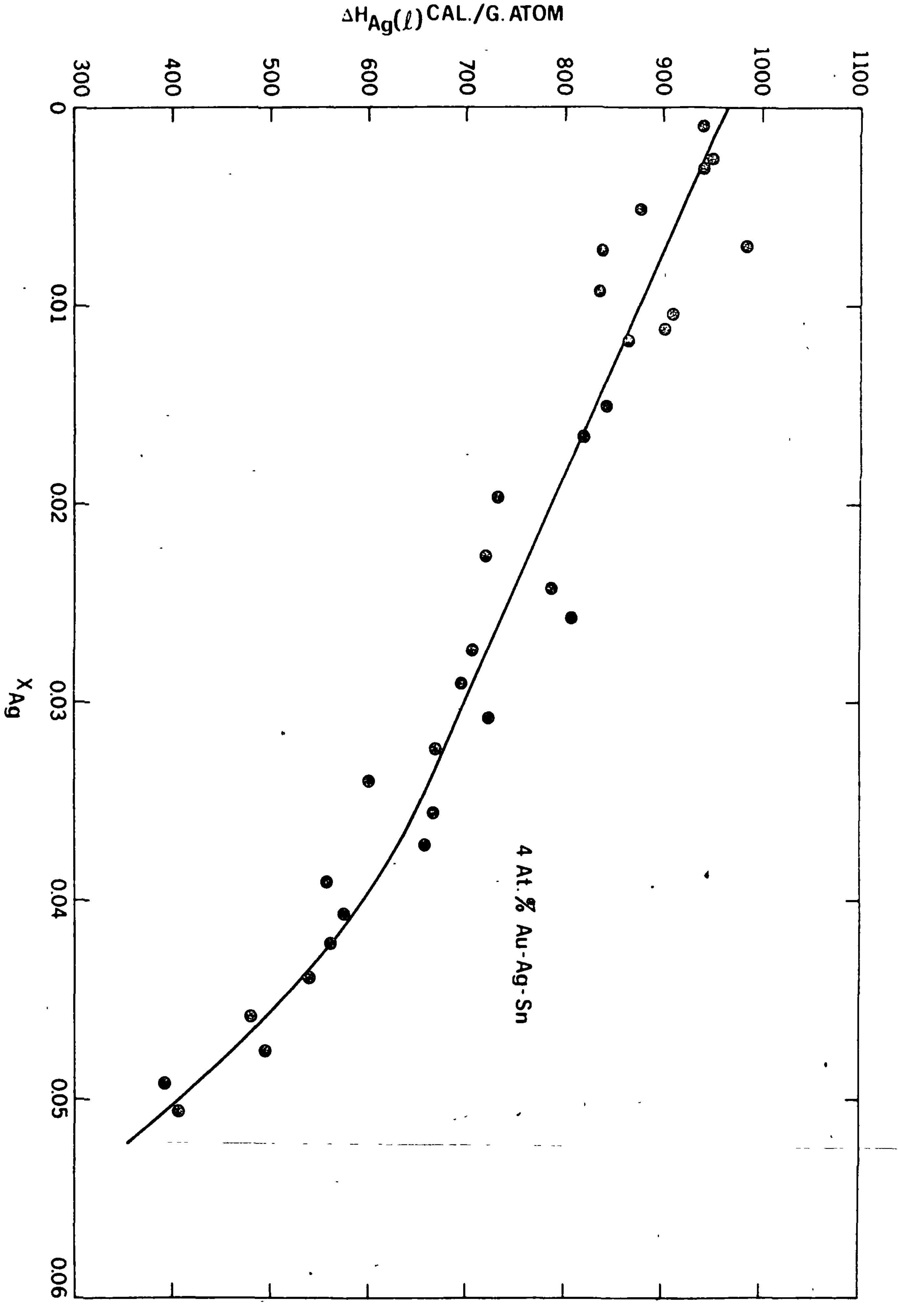
LIST OF FIGURES


-8300
-8200
-8100
-8000
-7900
-7800
-7700
$\overline{\Delta H}_{Au}(\ell)$ CAL./G. ATOM
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
X_{Au}
4 at.%Ag-Au-Sn
Au-Sn


1100
1000
900
800
700
600
500
400
300
$\overline{\Delta H}_{Ag}(\ell)$ CAL. / G. ATOM
0
0.01
0.02
0.03
0.04
0.05
0.06
X_{Ag}
Ag-Sn


RANDOM SOLUTION MODEL
● POOL
▲ ORIANI & MURPHY
○ PRESENT WORK
TEMP. °K
650
660
670
680
690
700
710
720
730
740
750
760
Ω_{Ag} CAL./G. ATOM
0
2000
4000
6000
8000
10000
12000
14000
16000


$\Delta\bar{H}^{o}_{Au(\ell)}$ CAL / G.ATOM
8200
8150
8100
8050
8000
0
0.01
0.02
0.03
0.04
0.05
x_{Ag}
η^{Ag}_{Au} = -2650 CAL./G. ATOM


ΔH$_{Ag(\ell)}$ CAL./G. ATOM
300
400
500
600
700
800
900
1000
1100
X$_{Ag}$
0
0.01
0.02
0.03
0.04
0.05
0.06
4 At.% Au-Ag-Sn