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A CALORIMETRIC STUDY OF LIQUID GOLD-TIN ALLOYS NEAR THE COMPOSITION AuSn

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Thesis

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Jean-Louis Daniel Guy Masse

(Master's Thesis)

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ABSTRACT

The relative partial molar enthalpies of gold and tin in liquid gold-tin alloys have been measured by liquid metal solution calorimetry at a temperature just above the congruent melting point of AuSn from $x_{Sn} = 0.475$ to $x_{Sn} = 0.510$. The results are represented, within a maximum scatter of ± 20 cal/g atom, by two curves which do not reveal any anomalous behavior at the equiatomic composition. The data are discussed in relation to existing X-ray diffraction studies of the liquid and are compared with previous thermodynamic measurements.

Jean-Louis Daniel Guy Masse, is a graduate student completing a Masters degree in the Department of Mineral Technology, College of Engineering, and Inorganic Materials Research Division, Lawrence Radiation Laboratory, University of California, Berkeley, California.

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INTRODUCTION

There has been some success achieved in relating measured thermodynamic properties of solid intermetallic systems to the behavior of other physical and chemical properties or to configurational and distributional factors. Some examples of such correlations are studies relating thermodynamic data to ordering phenomena in the Au-Cu system,[1] to magnetic effects in Ag-Pd[2] and Cu-Pd[3] alloys and to structural modifications in AgZn.[4] For liquid phases, however, there has been much less progress. Thermodynamic properties for liquid intermetallic phases have generally been measured over broad composition ranges and a smooth curve is most often assumed to represent the variation of properties with composition. There has been little effort to examine in minute detail over relatively small ranges of composition the variation of properties which might sensitively test the validity of structural hypotheses inferred from other types of measurements.

The object of this investigation was to study liquid gold-tin alloys near the equiatomic composition, slightly above the congruent melting temperature of AuSn, by measuring in close detail the compositional variations of the relative partial molar enthalpies of gold and tin. A sketch of the phase diagram taken from Hansen[5] is shown in Fig. 1. The AuSn phase exists over a very narrow range of homogeneity with a congruent melting temperature of 691°K. This solid phase has been shown to have the completely ordered NiAs structure.[5]

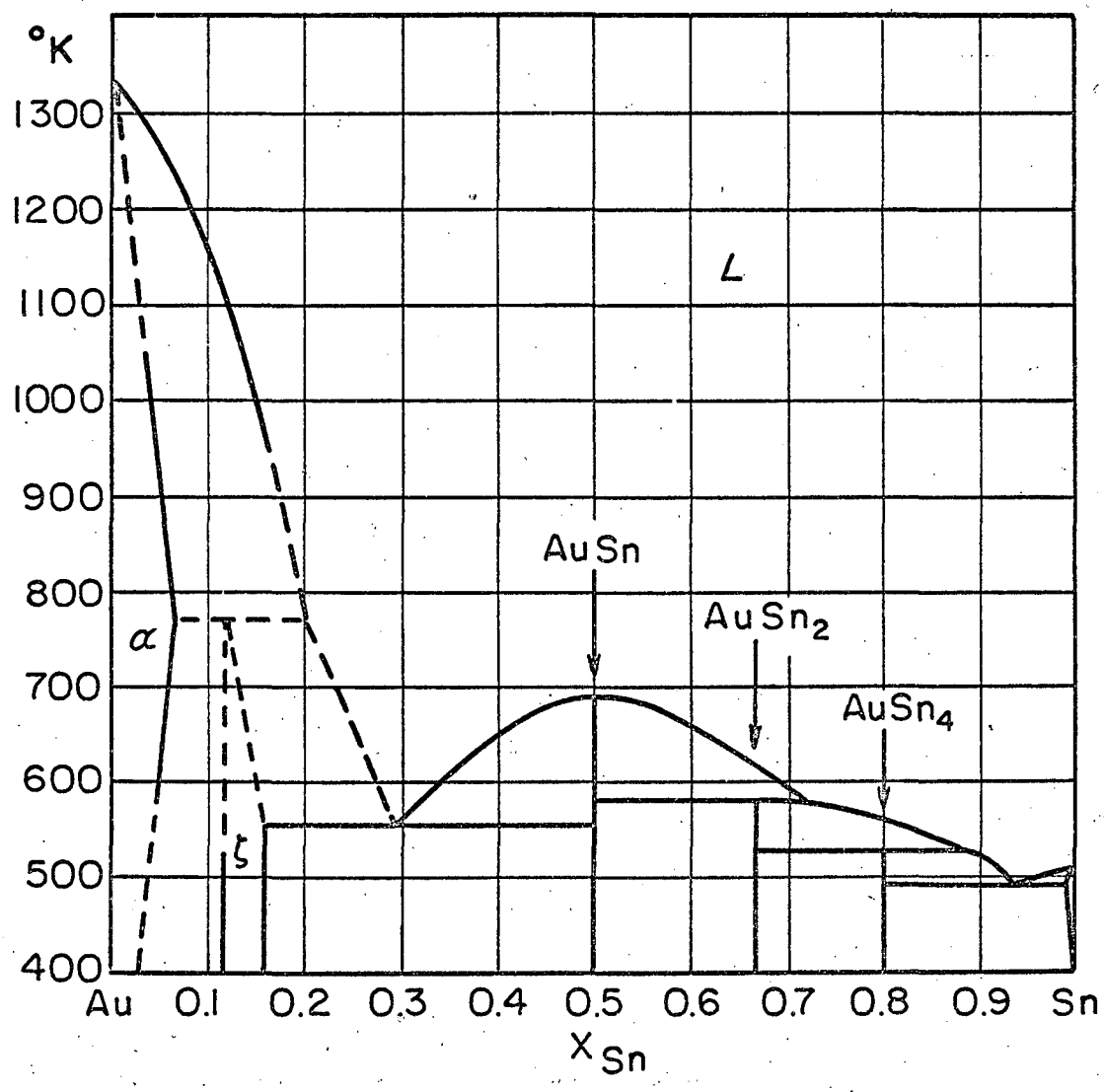

FIG. I PHASE DIAGRAM OF THE Au-Sn SYSTEM.

An evaluation of existing thermodynamic data for the Au-Sn system has been made by Hultgren et al.[6] The heats of formation of the solid and liquid phases are highly exothermic indicating the high relative stability of the Au-Sn bond.

X-ray diffraction studies of liquid Au-Sn alloys at several compositions and temperatures were made by Hendus,[7] who measured the diffraction intensity as a function of the diffraction angle. For the equiatomic composition at 713° K, the first maximum in the intensity curve showed a double peak, the first falling at the mean value of the highest peaks for pure gold and pure tin, and the second corresponding closely to the lattice spacing of the [012] planes in solid AuSn which yield the maximum intensity reflexions for that phase. At 813° K, the second peak had a much lower intensity, while the first was relatively unchanged. This behavior was not found for the other alloys studied, at 16.3 and 29.4 at.% Sn. These results were interpreted by Hendus as suggesting the possible existence of some degree of residual crystalline order in the equiatomic liquid alloy at temperatures near the congruent melting point.

Measurements of the variation of partial molar enthalpies and entropies with composition offer probably the most sensitive thermodynamic method for detecting corresponding compositional changes in the degree of order as pointed out by Wagner.[8] This is well illustrated for a solid phase by the variation of the relative partial

molar heat contents of gold and copper in the highly ordered AuCu phase[6] as shown in Fig. 2. For the ordered phase at 653° K, the partial molar quantities are seen to change very sharply on passing through the composition at which the degree of order is a maximum. The present measurements were undertaken to determine whether a similar behavior could be detected for liquid Au-Sn alloys at and near the equiatomic composition, thus adding confirmation to the hypothesis of pseudo-crystalline order made by Hendus.

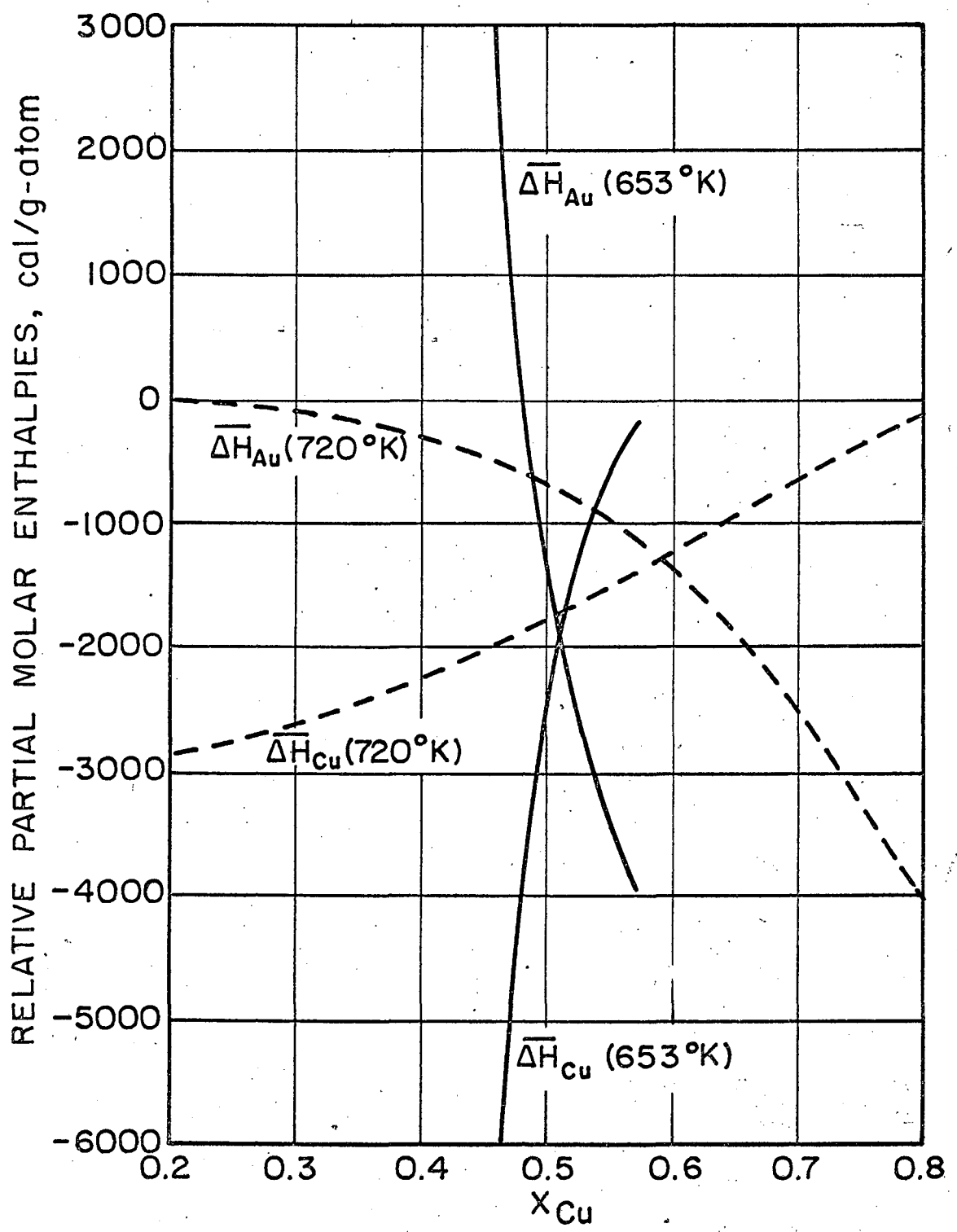

FIG. 2 RELATIVE PARTIAL MOLAR ENTHALPIES OF GOLD AND COPPER IN Au - Cu ALLOYS.

EXPERIMENTAL PROCEDURE

Materials

The gold used for this investigation was obtained from Engelhard Industries Inc., Newark, New Jersey; the tin from Vuncan Detinning Company, Sewaren, New Jersey. Each was reported to be 99.99+ per cent pure.

Preparation of the alloy

The gold-tin alloy was prepared by melting the pure metals into the molybdenum crucible used in the calorimetric measurements. The metals were carefully weighed and melted together at about 720° K in an evacuated pyrex tube heated in a vertical tube furnace. A reweighing showed the loss in weight on melting to be less than 0.06 per cent. The weight of the alloy was 410.20 g. with a composition of 49.953 at. % Sn, calculated from the amounts of gold and tin used. The molybdenum crucible weighed about 116 g.

Calorimetry

A liquid metal solution calorimeter, described in detail previously,[9] was used for measurements of the partial molar heat contents. A schematic drawing of the apparatus is shown in Fig. 3. The liquid alloy contained in the molybdenum crucible (A) is stirred by a molybdenum impeller attached to an alundum shaft. The crucible is surrounded by a chrome-plated copper jacket (B) weighing about ten kilograms. The jacket is heated by a continuous nichrome heating element wound on

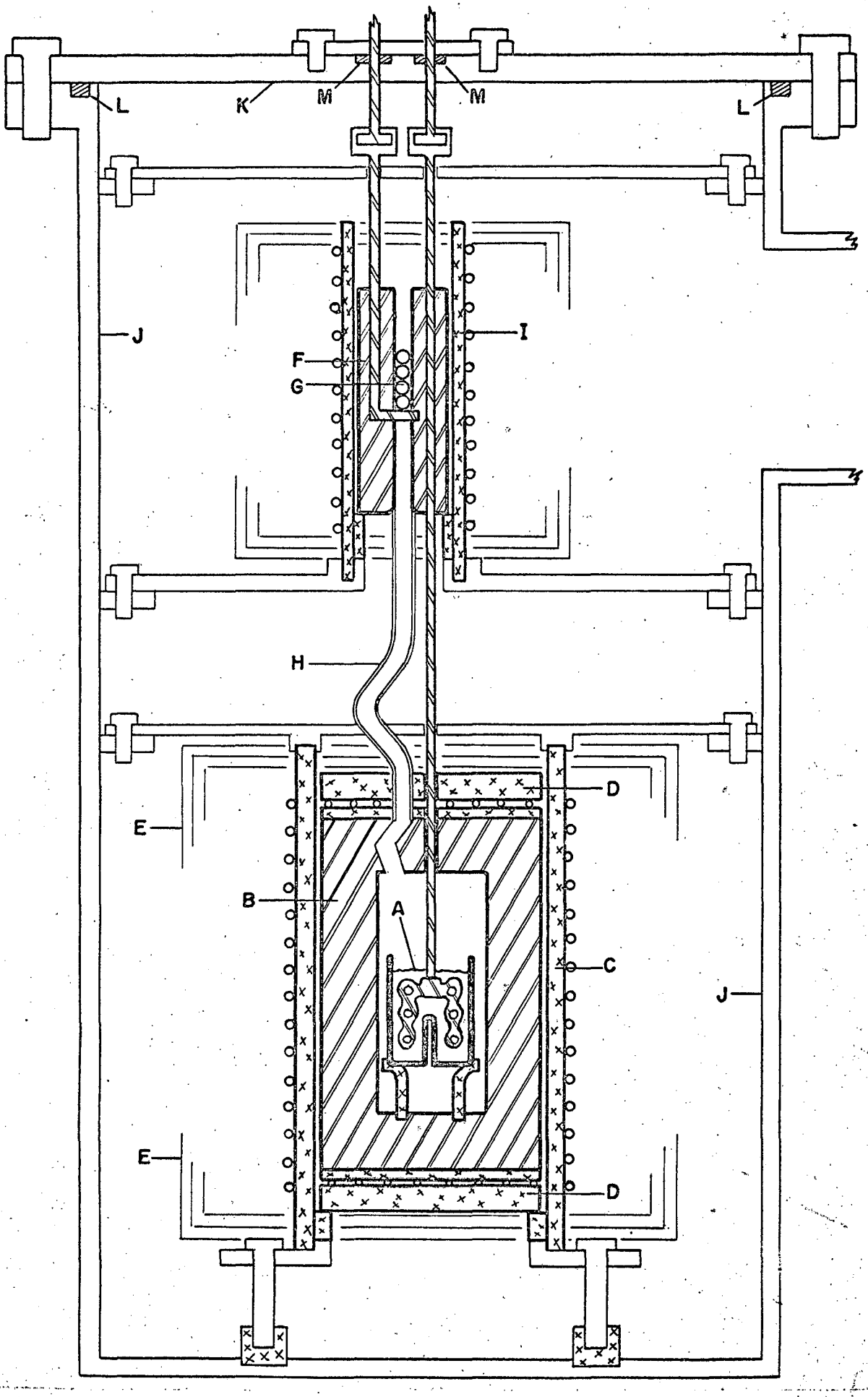

FIG. 3 LIQUID METAL SOLUTION CALORIMETER.

an alundum tube (C) at the sides and ceramic disks (D) at the ends of the jacket. Externally caused temperature drifts or fluctuations in the jacket before or during a run are prevented by means of a sensitive resistance thermometer controller, through which it is easily possible to obtain constancy of the calorimeter temperatures to within less than 0.001° C before making a run. Radiation shields (E) provide insulation from the rest of the apparatus.

The temperature of the bath is measured by means of a 30 gauge copper-constantan thermocouple extending up a well in the bottom of the crucible, and that of the jacket by a couple located in a vertical hole near the jacket wall ending at a point opposite the crucible. The two couples have a common constantan leg. The jacket temperature is measured by a platinum-platinum plus ten per cent rhodium couple. The thermocouples were calibrated at the melting point of AuSn (691° K) by means of heating and cooling curves. Thermocouple e.m.f.'s are measured on a shielded White double potentiometer in connection with a moving coil reflecting galvanometer, meter scale, and telescope. The sensitivity is such that a scale deflection of one mm. corresponds to a change of about 0.015 μV or 0.00024° C in the reading of the differential couple. The upper part of the apparatus contains the dispenser unit (F) from which the specimen (G) can be ejected, after having been preheated by the furnace (I) if desired, through a Vycor glass tube (H) into the bath. A thermocouple measures

the specimen temperature prior to the drop. The units of the apparatus are supported in a vacuum-tight, water-cooled shell (J), which is evacuated to a pressure of about 10^{-6} mm of mercury during the measurements. Vacuum tightness is obtained by means of three O-ring seals; one (L) for the lid (K) and two (M) for the stirrer and the dispenser.

The energy equivalent of the calorimeter was determined several times in the course of the experiment by measuring the temperature drop accompanying the addition of a specimen of tungsten and using the known heat content data for tungsten taken from Hultgren et al.[6]

This investigation reports the results of 54 measurements of the relative partial molar heat contents of gold and 45 measurements for those of tin. The bath was maintained at about 696° K for all the runs, at which temperature gold and tin dissolve in about one minute. The specimens of pure gold and pure tin were dropped from the temperature of the dispenser unit which received heat from the calorimeter furnace, about 318° K-322° K. The average gold specimens weighed about 0.7 g and those of tin about 0.4 g. The measured heat contents were evaluated from the temperature change accompanying solution of the specimens corrected for the heat transfer between crucible and jacket during the reaction period, made assuming Newton's law of heat transfer as has been discussed previously.[9]

EXPERIMENTAL DATA

The experimentally determined partial molar enthalpies of gold and tin are presented in Tables I and II. The measured values have been referred to solid gold and liquid tin respectively at the solution temperature, using the heat content data for gold and tin tabulated by Hultgren et al.[6] The composition of the bath for each run has been taken as the average between the compositions before and after the run. The results are also shown plotted in Fig. 4.

The partial molar enthalpies are all exothermic and show excellent precision with a maximum scatter of about ± 20 cal/g atom for any composition. The smooth curve shown in Fig. 4 was selected for the values for tin. It fits the equation

$$(\overline{H}_{Sn} - H^{\circ}_{Sn(\ell)})_{696^{\circ}K} = (-15324 + 11167\,x_{Sn})(1 - x_{Sn})^2 \qquad (1)$$

which is of the form predicted by sub-regular solution behavior. The Gibbs-Duhem integration of this equation, choosing from the data the constant of integration so that $\overline{H}_{Au} - H^{\circ}_{Au(s)} = -486$ at $x_{Sn} = 0.49$, gives the equation

$$(\overline{H}_{Au} - H^{\circ}_{Au(s)})_{696^{\circ}K} = 3220 - 20907\,x^2_{Sn} + 11167\,x^3_{Sn} \qquad (2)$$

which is shown by the smooth curve for the Au data. As can be seen, the experimental points agree remarkably well with both curves, hence they obey the Gibbs-Duhem relationship.

TABLE I

Measured partial molar enthalpies of tin at 696° K

Run no.	x_{Sn}	$\bar{H}_{Sn} - H^{\circ}_{Sn(\ell)}$ cal/g atom	Run no.	x_{Sn}	$\bar{H}_{Sn} - H^{\circ}_{Sn(\ell)}$ cal/g atom
102	.4748	-2753	139	.4980	-2460
103	.4756	-2753	140	.4987	-2459
106	.4770	-2735	141	.4993	-2445
107	.4777	-2729	5	.4998	-2427
108	.4785	-2702	142	.5000	-2429
109	.4792	-2708	6	.5005	-2432
110	.4800	-2689	143	.5006	-2431
114	.4819	-2666	7	.5012	-2412
117	.4839	-2642	145	.5013	-2424
118	.4846	-2640	8	.5019	-2409
119	.4854	-2628	146	.5019	-2411
122	.4874	-2596	9	.5025	-2404
125	.4888	-2573	147	.5025	-2396
126	.4895	-2569	10	.5030	-2399
127	.4902	-2565	11	.5035	-2391
129	.4916	-2551	12	.5041	-2371
130	.4924	-2533	13	.5047	-2367
131	.4932	-2525	16	.5060	-2362
133	.4947	-2501	17	.5066	-2344
135	.4954	-2503	19	.5077	-2325
136	.4960	-2485	21	.5090	-2309
137	.4966	-2490	23	.5102	-2294
138	.4973	-2466			

TABLE II

Measured partial molar enthalpies of gold at 696° K

Run no.	x_{Sn}	$\bar{H}_{Au} - H^{\circ}_{Au(s)}$ cal/g atom	Run no.	x_{Sn}	$\bar{H}_{Au} - H^{\circ}_{Au(s)}$ cal/g atom
100	.4747	-291	65	.4954	-557
99	.4755	-312	64	.4960	-578
97	.4772	-319	63	.4967	-573
96	.4778	-322	62	.4974	-582
93	.4797	-343	61	.4980	-599
92	.4803	-369	60	.4989	-609
91	.4810	-369	59	.4993	-616
90	.4818	-380	153	.4996	-623
88	.4826	-396	58	.5000	-624
87	.4834	-411	152	.5004	-637
86	.4842	-409	56	.5007	-622
85	.4849	-417	151	.5011	-650
84	.4857	-435	55	.5012	-631
83	.4864	-448	150	.5018	-649
82	.4872	-451	53	.5018	-635
81	.4879	-456	149	.5024	-664
80	.4884	-468	51	.5033	-664
76	.4897	-478	50	.5040	-671
75	.4902	-482	48	.5054	-681
74	.4908	-501	47	.5060	-695
73	.4913	-512	45	.5067	-692
72	.4919	-512	44	.5074	-713
71	.4924	-516	43	.5081	-707
70	.4930	-526	42	.5087	-724
68	.4936	-537	41	.5094	-744
67	.4942	-545	40	.5102	-756
66	.4948	-546	39	.5108	-762

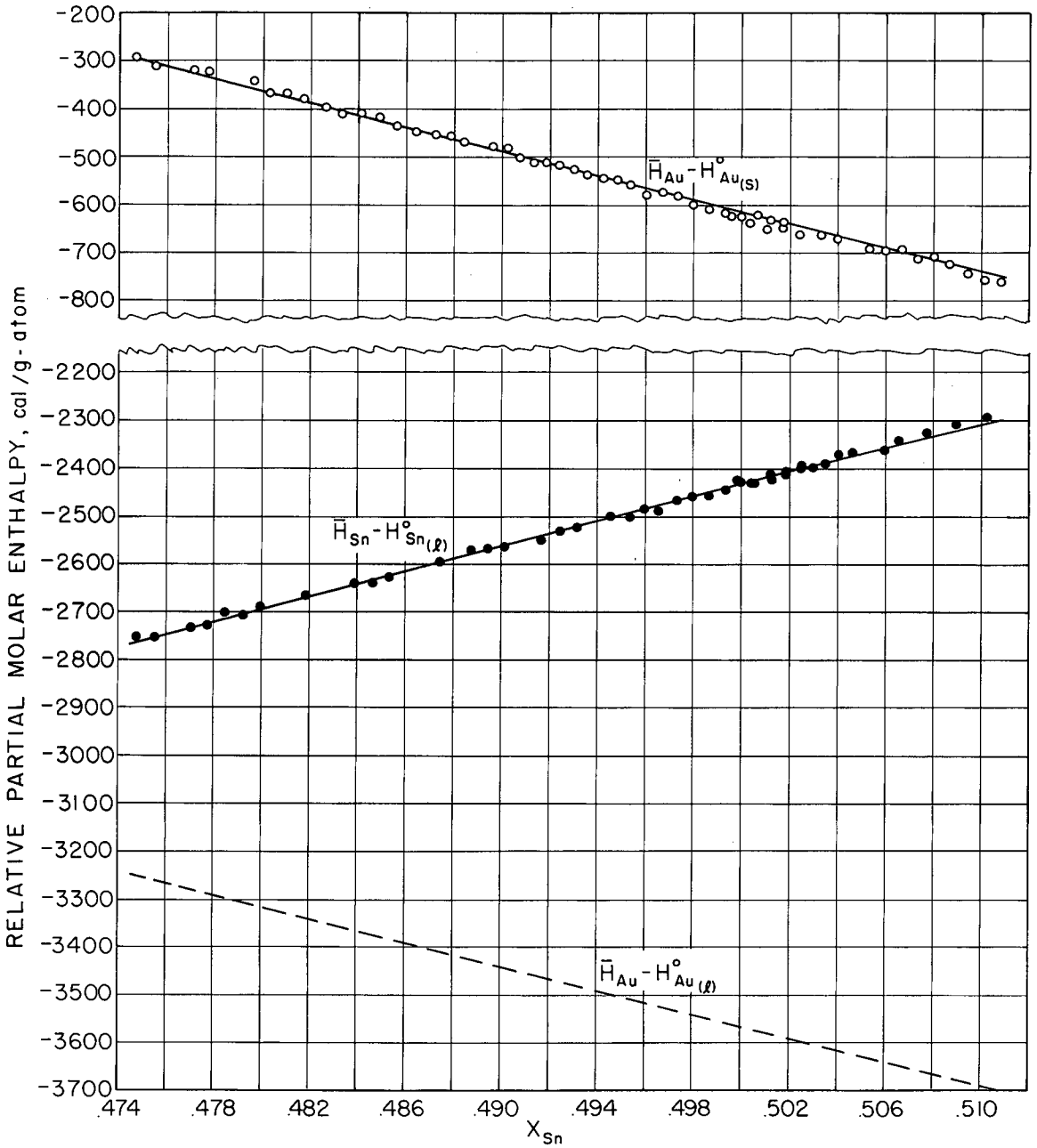

FIG. 4 RELATIVE PARTIAL MOLAR ENTHALPIES OF GOLD AND TIN IN LIQUID GOLD-TIN ALLOYS AT 696 °K.

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DISCUSSION

The tabulated partial molar enthalpies of gold are referred to solid gold as the reference state. In order to refer them to supercooled liquid gold as the reference state, it is necessary to subtract from the tabulated values the heat of fusion of gold at 696°K. However, supercooled liquid gold at that temperature is a hypothetical state; to estimate it, it is necessary to make some assumption regarding the heat capacity of supercooled liquid gold between 696°K and the normal melting point of 1336°K. In their evaluation of data for the Au-Sn system Hultgren et al.[6] have taken the heat of fusion as being independent of temperature and thus the heat of fusion at 696°K would be the same as that at the melting point, i.e., 2955 cal/g atom. Making that same assumption to refer the results to supercooled liquid gold, the dashed curve for $(\overline{H}_{Au} - H^{\circ}_{Au(\ell)})$ shown in Fig. 4 is obtained. The resulting value at $x_{Sn} = 0.500$ is $(\overline{H}_{Au} - H^{\circ}_{Au(\ell)}) = -3571$ cal/g atom. Combining this with the value of $(\overline{H}_{Sn} - H^{\circ}_{Sn(\ell)}) = -2435$ cal/g atom, yields a value of -3003 cal/g atom for the integral heat of formation of the liquid equiatomic alloy from the liquid components at 696°K. Considering the precision of the measurements, possible thermocouple errors and errors in the assumed heat content of tungsten, etc., the maximum uncertainty should not exceed ±50 cal/g atom. However, this value is 300 calories more exothermic than that tabulated for 700°K by Hultgren et. al.[6] That value is based upon the heat of formation measurements of solid

AuSn at 273° K by Bever et al.,[10] and the heat content measurements for the solid and liquid alloy between 273° K and 700° by Kubaschewski.[11] It is difficult to account for the discrepancy. Certainly further determinations should be made of heats of formation and heat contents of AuSn.

A different value for the heat of fusion of pure gold at 696° K would be obtained by assuming $(\bar{H}_{Au} - H^{\circ}_{Au(\ell)})$ to follow a sub-regular solution behavior as represented by the last two terms of Equation (2):

$$(\bar{H}_{Au} - H^{\circ}_{Au(\ell)})_{696^{\circ}K} = -20907x^2_{Sn} + 11167x^3_{Sn} \qquad (3)$$

This leads to a heat of fusion at 696° K of 3220 cal/g atom, which would mean that the average heat capacity of supercooled liquid gold between 696° K and 1336° K is lower than that of solid gold over the same range of temperature.

The corresponding equation for the integral heat of formation from the liquid components, assuming 3220 cal/g atom as the heat of fusion of gold at 696° K, is calculated from Equations (1) and (3) as:

$$\frac{\Delta H}{x_{Au}x_{Sn}} = -15324 + 5584x_{Sn} \qquad (4)$$

As can be seen from the curves of Fig. 4, the partial molar heat contents of gold and tin do not show any anomalous variation at the equiatomic composition, but vary smoothly throughout the measured

range. The slopes of the curves are not particularly large. In fact, if the sub-regular solution behavior represented by Equation (4) is assumed valid over the entire composition range, a smooth curve, shown in Fig. 5, is obtained which is of the same general shape as the one selected by Hultgren et al.,[6] at 873° K.

The results found do not necessarily invalidate the conclusions drawn from X-ray observations by Hendus. The absence of any anomalous behavior in the partial molar heats at the equiatomic composition could result from either of two factors:

(1) The energy effect of the ordering is too small to be detected by the present calorimetric measurements, even though they would seem to be the most sensitive that could be employed.

(2) The ordering phenomena suggested by Hendus occur over a wide range of composition, thus making only a slowly varying exothermic contribution to the heat of formation.

Measurements of the partial molar heats at the equiatomic composition as a function of temperature would be valuable, since the degree of order might change more rapidly with temperature than with composition. Viscosity[12] and resistivity measurements as a function of temperature and composition might also reveal more of the structure of the liquid AuSn phase.

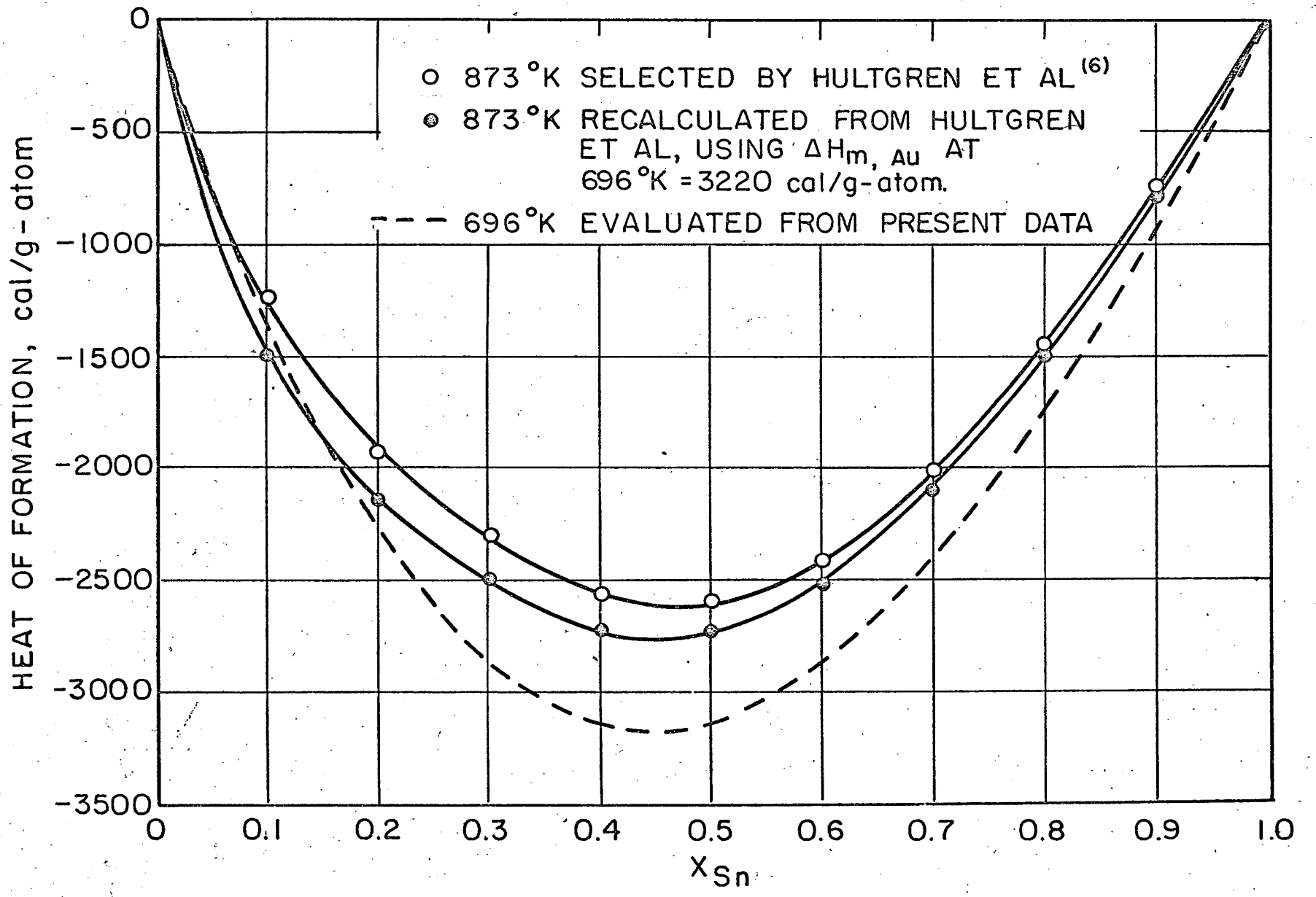

FIG. 5 HEATS OF FORMATION OF LIQUID GOLD-TIN ALLOYS.

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