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J. D. G. Masse, R. L. Orr, and Ralph Hultgren

ABSTRACT

The relative partial molar enthalpies of gold and tin in liquid gold-tin alloys have been measured from x_{Sn} = 0.474 to 0.510 at 696°K, slightly above the melting point of solid AuSn. Within an average precision of 6 cal/g-atom, the data are represented by two smooth curves, which satisfy the Gibbs-Duhem relationship and which do not show any anomalous behavior in the range of composition studied. The results give no support to the hypothesis that atomic associations in the equiatomic liquid alloy resemble those in solid AuSn.

Little has been firmly established as to the nature of atomic distri-
bution in liquid metallic phases. A favored hypothesis assumes the
existence of atomic groupings in the liquid phase which are similar to
those in solid phases occurring at lower temperatures. Beginning with
this hypothesis, it is often possible to adjust the values of certain parameters
(such as degree of association) so that approximate agreement is achieved
with certain features of the X-ray diffraction pattern of the liquid; even
though many other possible structures might satisfy the data equally well.
Thus, in this manner, the structure of liquid tin has been described as
a dispersion of fragments of gray tin in a matrix of metallic tin. [1]

Four X-ray diffraction studies[2-5] have been made of the liquid alloy
of composition AuSn at temperatures slightly above the melting point of
the solid. Each investigator concluded, on somewhat different grounds,
that the liquid consisted to a large extent of arrays of atoms similar to
the solid, with admixture of more disordered arrays. Solid AuSn has the
nickel arsenide crystal structure: each Sn atom has six nearest neighbors,
all Au atoms; and each Au atom has six Sn and two Au atoms as nearest
neighbors. It remains highly ordered to the melting point. The liquid
alloy has a large exothermic ($\Delta H_{700°K}$= -2700 cal/g-atom[6]) enthalpy of
formation, favoring ordering and making the hypothetical molecular
association not unreasonable.

The possible existence of such solid-like arrays, or of a high degree
of order that occurs preferentially at a specific composition in a liquid alloy,
might also be revealed by thermodynamic behavior somewhat analogous to

that in highly ordered solid alloy phases. The latter often exist over wide composition ranges, within which the highest degree of order occurs at the ideal composition for which the atomic fractions are equal to the fractions of sites which are "right" for each kind of atom. On departing from the ideal composition, the excess atoms occupy "wrong" positions, raising the internal energy and making it progressively easier for additional atoms to occupy "wrong" positions. Thus, on either side of the ideal composition, there should be a pronounced rise in the entropy and enthalpy, which would be shown particularly by the change in the relative partial molar enthalpies, $\Delta \overline{H}_i$, since they depend strongly on $d\Delta H/dx$.

In the one case where accurate measurements have been made, the solid AuCu ordered phase, the structure becomes much less ordered as the composition deviates from the ideal, and relative partial molar enthalpies change sharply as shown by the data[6] given in Table I.

Table I. Integral and Partial Molar Enthalpies of Formation at 653°K of Solid Gold-Copper Alloys near the Composition AuCu

x_{Cu}	ΔH	$\Delta \overline{H}_{Au}$	$\Delta \overline{H}_{Cu}$
	calories/gram atom		
0.48	-1858	- 20	-3850
0.50	-1902	-1405	-2400
0.52	-1897	-2360	-1470

This suggests the possibility of finding similar pronounced changes in the relative partial molar enthalpies of gold and tin in liquid alloys near the composition AuSn if the postulated solid-like arrays[2-5] were present.

The present paper reports the results of direct calorimetric measurement of these quantities at close intervals from x_{Sn} = 0.474 to 0.510, at 696°K, just 5 degrees above the melting point of solid AuSn.

EXPERIMENTAL

The gold and the tin used were each reported to be 99.99+pct pure. They were melted together under vacuum at 720°K directly into the molybdenum container which is the heart of the calorimeter. Loss of weight on melting was 0.06 pct; the final alloy weighed 410.20g. Assuming the entire loss was tin, the final composition was x_{Sn} = 0.4995.

A short description of the liquid metal calorimeter will suffice, since it has been more fully described elsewhere.[7] The molybdenum container sits on three refractory points in a vacuum and is completely surrounded, except for necessary small openings, by a large copper block. Differences in temperature between container and block are read to a sensitivity of 0.0003° by means of a 30 gage differential copper-constantan thermocouple connected to a White double potentiometer. Absolute temperatures are measured by a platinum-platinum+10 pct rhodium thermocouple located in the block. Temperatures of the block are held constant to 0.001°K by a Wheatstone bridge controller with a platinum resistance thermometer sensing element. The metal is stirred with a molybdenum stirrer. After temperatures have been stabilized for 24 hours and the differential temperature remains constant within ±0.001°K for at least 20 min., the calorimeter is ready to operate.

A sample, usually weighing less than 1g, is then dropped into the

metal bath, and the resulting displacement in temperature, ΔT, is followed by readings of the differential thermocouple at short intervals of time, t. After the reaction is over (in this research in about 1 min), the calorimeter returns to its initial temperature according to Newton's law, $d \log \Delta T/dt = k$, from which the value of the coefficient k is determined. The total heat effect in dissolving the sample is calculated from the temperature displacement and the heat capacity of the calorimeter, plus a correction for heat flow calculated using the measured value of k. The heat capacity is determined frequently during the runs by dropping samples of tungsten into the liquid alloy.

The samples of pure gold and pure tin were of such a size that the composition of the gold-tin liquid was displaced about 0.06 at. pct by each addition. This displacement is so small that the heat effect (after correction for the sensible heat required to raise the sample to the bath temperature) may be taken as the relative partial molar enthalpy of the component added at the average alloy composition for the run.

Tin samples were added until the composition of the bath reached $x_{Sn} = 0.5108$. Then gold samples were added until $x_{Sn} = 0.4747$; following which tin samples were added to $x_{Sn} = 0.5025$; then five more gold samples were added, to a final composition $x_{Sn} = 0.4990$. In all, 45 determinations were made of the relative partial molar enthalpies of tin and 54 of gold.

RESULTS

The results of the measurements are plotted in Fig. 1. The average precision is excellent, ± 6 cal/g-atom from the plotted curves, with a

maximum deviation of 20 cal/g-atom. Over the range of measurement

the curves fit the equations:

$$\left.\begin{array}{l}(\overline{H}_{Sn} - H^{\circ}_{Sn(\ell)})_{696^{\circ}K} = (-15324 + 11167x_{Sn})(1-x_{Sn})^2 \\[2mm] (\overline{H}_{Au} - H^{\circ}_{Au(s)})_{696^{\circ}K} = 3220 - 20908x_{Sn}^2 + 11167x_{Sn}^3 \end{array}\right\} (0.474 < x_{Sn} < 0.510)$$

These equations bear the Gibbs-Duhem relationship to each other, which

provides a valuable proof of the consistency of the measurements. From

these expressions, the integral enthalpy of formation of the liquid alloy

from solid gold and liquid tin is given by

$$\Delta H = 3220 - 18544x_{Sn} + 20908x_{Sn}^2 - 5584x_{Sn}^3 \qquad (0.474 < x_{Sn} < 0.510)$$

For comparisons with published values it is desirable to refer the

results to a hypothetical liquid gold for which the heat of fusion, 2955

cal/g-atom, is invariant with temperature.[6] Thus, with respect to liquid

gold, the values of $\Delta\overline{H}_{Au}$ are more exothermic by 2955 cal/g-atom, and

the integral enthalpies of formation are more exothermic by $(1-x_{Sn})$ 2955

cal/g-atom. On this basis the enthalpy of formation for the reaction

$$0.5Au_{(\ell), 696^{\circ}K} + 0.5Sn_{(\ell), 696^{\circ}K} = Au_{0.5}Sn_{0.5(\ell), 696^{\circ}K}$$

is $\Delta H = -3000$ cal/g-atom. The tabulated value,[6] -2700 cal/g-atom, was

derived from the enthalpies of formation of solid AuSn, measured at 273°K

by Misra, Howlett and Bever,[8] and at 623°K by Kleppa,[9] both by tin solution

calorimetry, and from the enthalpy increment data of Kubaschewski.[10]

The discrepancy of 300 cal/g-atom, much larger than the uncertainty in

the present results, indicates further investigation is needed.

DISCUSSION

The relative partial molar enthalpies of gold and tin change smoothly

with composition, with no special features at $x_{Sn} = 0.50$ or at any other

composition within the range studied. The rate of change with composition

is moderate and is not greater than would be expected in a solution in which atoms were randomly distributed. In contrast, in the highly ordered AuCu phase, for which properties are listed in Table I, the partial molar quantities change five times as fast as in the gold-tin liquid alloy investigated.

The present data give no support to the hypothesis that atomic associations in liquid AuSn just above the melting point resemble those in the solid phase. On the contrary, the data strongly indicate that there is no sharp change in the nature of the atomic distribution on passing through the equiatomic composition, where such associations should have the largest probability of occurence. This in turn suggests that the degree of ordering is not high and that it changes smoothly with composition. A moderate degree of short-range order expected in exothermic systems may well behave in this way.

A further indication that the liquid alloy is not highly ordered is provided by the high entropy of melting of AuSn (ΔS_m = 4.40 cal/deg g-atom[6]). For most metallic elements (which are close packed or nearly so), $\Delta S_m \approx 2.3$ cal/deg g-atom. For ionic compounds, which surely must be ordered in the liquid so that positive and negative ions surround each other, $\Delta S_m \approx 3$ cal/deg g-atom. (Thus for NaF, NaCl, NaBr, NaI, KF, KCl, MgO, and CaO, ΔS_m = 3.1, 3.15, 2.95, 2.8, 3.0, 2.9, 2.9, and 2.1 cal/deg g-atom respectively[11]).

Although the present results do not absolutely disprove a moderate degree of association such as that hypothesized by the X-ray workers, they do cast considerable doubt on the validity of the conclusions. In fact, the X-ray diffraction data measure only an electron density distribution which

is the sum of the distributions about two kinds of atoms, A and B. The kinds of atoms producing the density cannot be directly identified. An analysis of the problem shows that the contributions of A and B could be separated only if patterns were obtained from three kinds of radiation,for each of which the relative scattering powers of A and B differed materially.[2] From differences of diffracted intensities, the interactions of A-A, B-B, and A-B could be separated. This has never been tried.

The usual X-ray diffraction pattern of a liquid alloy can hardly be expected to provide a unique description of the atomic distribution. Interpretations of such data for liquid gold-tin alloys indicating the presence of atomic groupings similar to those in solid AuSn are highly uncertain, since it has not been proved that other types of distribution would not account for the X-ray results equally well.

ACKNOWLEDGMENTS

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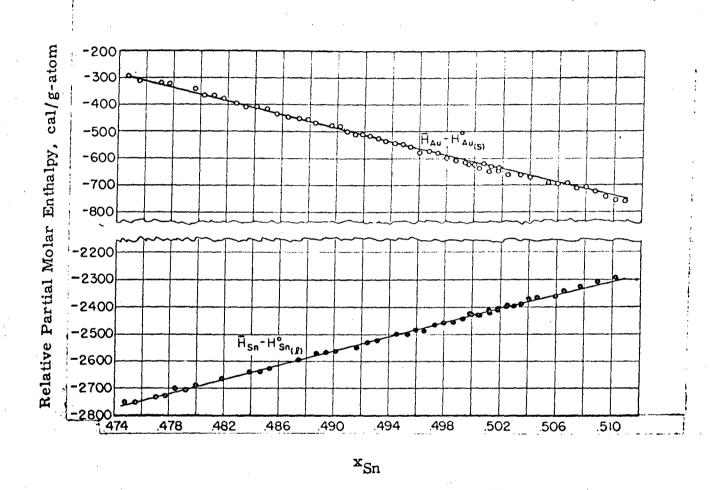
Fig. 1 Relative Partial Molar Enthalpies of Gold and Tin
in Liquid Gold-Tin Alloys at 696 °K