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SOME ENERGY MEASUREMENTS RELATED TO STRUCTURE OF METALLIC LIQUIDS

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Mechanisms of Melting and of Solidification
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In studies of atomic arrangements in liquid metals and alloys, a hypothesis frequently used as a starting point is that the immediate environments of atoms in the liquid state resemble those in the solid. For example, the structure of liquid tin has been described as consisting of tetrahedra of gray tin floating in a matrix of white tin fragments.[1]

Information on the structure of nonmetallic liquids makes this hypothesis seem reasonable. For organic crystals, complex molecules are often the basic unit of structure; the same molecules are the structural units of the liquid. In silica glass, presumably with the "frozen in" structure of liquid silica, each silicon atom has four oxygen neighbors at the corners of a regular tetrahedron, just as in crystalline silica. However, it is not at all obvious that these relations should hold for the metallic state. As we shall discuss below, interpretations of X-ray diffraction data purporting to show structural units in the liquid similar to those in the solid, are frequently questionable in the sense that other hypotheses would explain the data equally well. We suggest also that many inferences can be drawn from thermodynamic data as to the resemblance between liquid and solid atomic arrays.

X-RAY DIFFRACTION STUDIES

A number of high-temperature X-ray diffraction studies of liquid metals and alloys are beginning to appear. From Fourier analysis of the pattern, one can obtain for a metallic element a density of distribution of atoms about a central one as shown in Figure 1. The first peak indicates the most frequent distance of the nearest neighbors. The coordination number, or number of nearest neighbors to a central atom depends on how one defines nearest neighbor. Thus, one might decide that every atom nearer than the minimum close to 4Å should be recognized as a nearest neighbor. Generally, an attempt is made to complete the peak symmetrically on the far side, taking the area under the peak as proportional to the coordination number. The coordination number thus obtained depends considerably on the definition so that the values obtained by different workers may not be directly comparable.

Liquid metals are found to have high coordination numbers, ranging from 8 to nearly 12; sometimes the values given by different workers disagree considerably. For the distance of nearest neighbors, the results are less ambiguous; the distance is generally a few percent larger than in the solid state. Most metals are close-packed or body-centered cubic in the solid state; for these the liquid structure resembles the solid at least in coordination number and interatomic distance. For the less metallic non-close-packed metals such as bismuth and antimony, the coordination number in the liquid is considerably greater than in the solid, so the liquid structure does not resemble the solid.

Peaks on the distribution curve beyond the first one can be interpreted in

many ways and do little to precisely fix a structure describable in simple terms.

For binary alloys even the first peak cannot be unambiguously interpreted. The atomic distribution obtained is the superposition of densities about two kinds of atoms; the densities about atoms A and B cannot be separated from X-ray data alone. Moreover, it cannot be shown whether atoms under the first peak are A or B or a mixture of both. To resolve these questions and to obtain data as decisive as for pure metals would require three different diffraction patterns,[2] each from a radiation for which the relative scattering power of atoms A and B would differ significantly from the other two radiations.

It would seem that the best that could be done would be to show that the experimental pattern did or did not contradict an assumed distribution of atoms in the liquid without ruling out other hypothetical structures, which might differ substantially. This limitation is by no means recognized by a number of workers. For example, the eutectic liquid between Bi and InBi is asserted to have a structure consisting of InBi aggregates dispersed in atoms of Bi;[3] and the eutectic between In_2Bi and α-In solid solution, to consist of aggregates of In_2Bi and alpha.[4] In the latter case the author found that distributions of atomic In and Bi accounted for the X-ray data equally well, but he preferred the solid aggregate structure as being more in accord with the low viscosity of the eutectic composition liquid. Numerous similar assertions are found in the literature. As a further example we shall discuss liquid AuSn.

Solid AuSn has the NiAs structure in which each Sn is surrounded by 6 Au atoms while each Au is surrounded by 6 Sn and by 2 Au atoms. Four workers[2,5,6,7] concluded from their diffraction patterns that this distribution was found in the liquid together with dissociated atoms. However, one worker[8]

concluded that the liquid contained Au_3Sn aggregates along with Au and Sn atoms.

These examples show the unsatisfactory rigor of X-ray diffraction patterns in determining whether molecular associations exist in liquids. We suggest that energy measurements should be enlightening, though there are all too few thermodynamic measurements of liquid metallic phases of satisfactory accuracy. Pertinent data are (1) the entropy of melting, (2) heat capacity of liquids versus temperature, and (3) heat of formation versus composition of liquid alloys.

ENTROPY OF MELTING

The entropy of melting is an absolute measure of the disordering which occurs when a solid melts. Of course, the entropy includes all disordering, not just that of atomic arrangement. The nature of the bonding changes, for example. Probably the structural changes go along with electronic changes, however.

The entropy of melting of the elements depends greatly on the crystal structure in the solid state (Table 1). All the values quoted in Table 1 are experimental; other tables have been published which include estimated values which are only guesses. We hope in this paper to base our conclusions strictly on experimental values.

Metals with close packed crystalline structures (body-centered-cubic, face-centered-cubic, and hexagonal-close-packed) have low entropies of melting, indicating that the liquid resembles the solid. The more open crystalline structures, with a few exceptions, have much higher entropies of melting. The lanthanides and actinides are rather remarkable. Many of them undergo an allotropic transformation not far below the melting point with an unusually large

entropy of transformation. The resulting high temperature phases have very little mechanical strength and melt with the low entropies shown in the table. The high-temperature phases should be further investigated to understand why they resemble the liquid state more than the other solid phases. Ionic compounds of the NaCl structure also closely resemble the liquid (Table 2), in that their entropies of melting are of the order of 3 cal/deg g-atom.

To examine how the entropy of melting depends on the closeness of packing, we have calculated the packing ratio, defined as follows:

Packing ratio = actual density/close-packed density

The close-packed density is calculated from atomic radii given by Pauling[9] for coordination number 12, assuming a face-centered-cubic structure. Plotted against the packing ratio, the entropies of melting of many metallic elements fall near a straight line as shown in Figure 2. Clearly the more open the structure of the solid, the less it resembles the liquid. The atomic associations and reduced coordination numbers in these open solids are not carried over into the liquid states, which have higher coordination numbers similar to those of the close-packed solids.

For certain elements, such as Hg, Te, and especially Se and S, the entropies fall well below the line. This can be interpreted as indicating that some of the open solid structures are carried into the liquid.

The same treatment can be applied to alloys although there are serious difficulties in calculating the ideal close packed density. Should the radii of the atoms be averaged, or their volumes, or some other function? Also there is a good deal of indirect evidence that the radius of the atom in an alloy is not

the same as it is in the pure metal. We adopted the following procedure. Radii were averaged and a correction[10] for difference in electronegativity was applied:

$$\Delta r = >0.09\left|x_A - x_B\right| \quad \text{Angstroms}$$

where x_A and x_B are the electronegativities of the elements concerned.

This treatment is obviously not adequate, since some of the packing ratios turn out to be greater than 1. However, the results listed in Table 3 and shown in Figure 3 are still striking. Unordered alloys melt with an entropy approximately the same as the entropy of melting of metallic elements with the same packing ratio. Ordered alloys usually have a higher entropy of melting by an amount approximating the entropy of disordering. Thus it would seem that alloy liquids in general have atomic arrangements approximately close packed with the different species of atoms distributed randomly. Two ordered alloys (AuZn and CdSb) have entropies of melting corresponding to the disordered ones. This could be explained if they disordered before melting (data are lacking), or if there was order in the liquid state.

HEAT CAPACITY OF LIQUIDS

If atomic associations exist in liquid metals, it would be expected that they would break up with rising temperature. This process would contribute to the heat capacity; the greatest contribution might be just above the melting point, decreasing as the associations disappear.

Heat capacities of liquid metals are poorly known experimentally. In most cases the data consist of measurements of heat contents with a scatter so great that a straight line relationship with temperature implying a constant Cp is all that is justified. For some low-melting metals better measurements are

available,[11] as shown in Figure 4. It can be seen for all of these that, unlike solids, liquid heat capacities decrease with temperature for hundreds of degrees; in some cases it reaches a minimum and thereafter increases.

These data are perhaps consistent with molecular associations which break up slowly with rising temperature, though they hardly are proof of the existence of such associations, since other explanations are possible.[12] In some association models, the process is expected to take place much more rapidly. Bartenev,[13] for example, found that the Cp of liquid tin dropped 0.5 cal/deg g-atom within about 5° above the melting point, attributing it to the breakup of molecular aggregations. Our first experiments checked Bartenev's results very closely. However, when we repeated them with much purer tin, the sharp drop was entirely absent, though the data agreed at higher temperatures.

Eyring[12] has explained the slowly decreasing Cp of liquid metals as a gradual destruction of vibrational contributions to Cp, as the liquid comes increasingly to resemble a monatomic gas.

It can also be seen in Figure 4 that the Cp values for $Bi_{.50}In_{.50}$ and $In_{.53}Sn_{.47}$ trend with temperature in the same way as the elements. The anomalously high Cp just above the melting points in the alloys is no higher than in the elements. These measurements, which were made in our laboratory, are the only ones we have found for alloys in the liquid state.

HEATS OF FORMATION OF LIQUID ALLOYS

If the liquid alloy contains aggregates of atoms resembling those in a solid phase, it might be expected that the exothermic heat of formation would be unusually large at the composition of the solid phase. Investigators usually

find they can draw a smooth curve through heat of formation versus composition data which shows that this effect, if present, is not large compared with the scatter of the data. However, this by no means demonstrates there may not be small effects so that the curve in actuality dips downward near favored compositions. Such dips, if present, would have a large effect on the partial molar heat of formation of the liquid alloy, since the partial quantity depends strongly on the slope of the curve.

We studied the partial molar heats of Au and of Sn in liquids near the composition AuSn just above the melting point of that phase (Figure 5). As mentioned previously, many investigators deduced from X-ray diffraction data that this liquid contained many atomic aggregations resembling those in solid AuSn. In our measurements a liquid metal solution calorimeter was loaded with liquid near the AuSn composition.[14] The heat effect caused by the addition of a small sample of tin to the liquid measures directly the partial molar heat of solution of tin: the partial heat of gold is measured by adding gold. The results from the experiments are shown in Figure 6. Obviously, between the composition limits covered, there is no effect such as has been described; the composition AuSn is not a favored one.

DISCUSSION

X-ray diffraction data show that the metallic elements melt to form nearly closest packed arrangements of atoms in the liquid state, even in cases where the solid is not close packed. Conclusions that liquids contain aggregates resembling the solid phases are questionable.

The entropy of melting depends strongly on the crystal structure of the solid.

It increases as the solid becomes less closely packed, indicating the liquid is most like a close packed solid. For alloys the dependence on crystal structure is the same, except that ordered alloys have entropies of melting higher than the elements by an amount roughly equal to the entropy of disordering. Hence alloy liquids seem to consist of a random distribution of close packed atoms.

The heat capacity of liquid metals decreases with rising temperature for many hundreds of degrees. No indication is confirmed of pseudocrystalline aggregates which break up a few degrees above the melting point, though the data are not inconsistent with a hypothesis of aggregates which persist to high temperatures.

Although liquid AuSn has been reported to contain pseudocrystalline aggregates of solid AuSn, a highly sensitive study of its heat of formation showed that this composition was not especially favored energetically.

ACKNOWLEDGMENT

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Table 1. Available Data for Entropies of Melting of Elements*

Body-centered-cubic Structure

Element	T_m	ΔS_m
Cs	302	1.72
Rb	312	1.73
K	336	1.67
Na	371	1.68
Li	454	1.58
Tl	577	1.69
Ca	1123	1.75
Fe	1809	1.82

Hexagonal-close-packed Structure

Element	T_m	ΔS_m
Cd	594	2.46
Zn	693	2.55
Mg	923	2.32
Be	1560	2.25

Diamond Structure

Element	T_m	ΔS_m
Ge	1210	7.30
Si	1685	7.17

Face-centered-cubic Structure

Element	T_m	ΔS_m
Pb	601	1.91
Al	932	2.75
Ag	1234	2.24
Au	1336	2.21
Cu	1357	2.30
Ni	1725	2.44

Lanthanides and Actinides

Element	T_m	ΔS_m
Pu	913	0.74
Ce	1077	1.15
Nd	1297	1.32
Sm	1345	1.58
U	1405	2.20
Y	1803	1.52

Miscellaneous Structures

Element	Structure	Coord. No.	T_m	ΔS_m
Ga	Orth.	1	303	4.41
Te	Trig. A8	2	723	5.78
Bi	Rhomb. A7	3	544	4.77
Sb	Rhomb. A7	3	903	5.19
Sn	Tetr. A5	4(2)**	505	3.31
In	Tetr. A6	4(8)**	429	1.82
Hg	Rhomb. A10	6	234	2.34
Se	Trig. A8	2	494	2.63
S	Monocl.		392	0.75

* Units: T_m in °K, ΔS_m in cal/deg g-atom

** Number of second nearest neighbors (in parentheses) at only slightly greater distance than first

Table 2. Entropies of Melting of Ionic Compounds with the NaCl Structure

Compound	T_m, °K	ΔS_m, cal/deg g-atom
LiF	1121	2.88
NaF	1285	3.12
NaCl	1073	3.19
NaBr	1028	2.95
NaI	924	2.80
KF	1130	2.98
KCl	1043	2.92
FeO	1650	2.27
AgCl	728	2.12

Table 3. Packing Ratios and Entropies of Melting of Alloys

Alloy	Structure	Close-packed Density $\rho_{c.p.}$, gms/cm^3	Packing Ratio $\rho_{actual}/\rho_{c.p.}$	ΔS_m cal/deg g-atom
InSb	ord. fcc, zinc blende type (B3)	12.71	0.702	7.43
CdSb	ord. orthorhombic (B_e)	9.24	0.740	5.73
Mg_2Sn	ord. fcc, CaF_2 type (C1)	4.32	0.863	4.69
Bi_3Tl_2	disord. hexagonal (C32)	12.36	0.888	3.27
Mg_2Pb	ord. fcc, CaF_2 type (C1)	5.88	0.914	4.52
Au_3Ni_2	disord. fcc (A1)	17.51	0.921	1.98
Bi_2Mg_3	ord. hex., La_2O_3 type ($D5_2$)	7.14	0.928	3.98
$AuPb_2$	ord. bc tetr., Al_2Cu type (C16)	14.13	0.940	3.85
AuCd	ord. cubic, CsCl type (B2) (disord. before melting?)	14.59	0.944	2.27
Al_2Cu	ord. bc tetragonal (C16)	4.59	0.945	3.91
AuZn	ord. cubic, CsCl type (B2)	14.98	0.948	2.78
CuZn	disord. bcc (A2)	8.39	0.954	2.56
Al_3Mg_2	disord. fcc (A1)	2.33	0.955	2.60
Cd_3Cu_2	ord. bcc, γ-brass type ($D8_2$)	9.36	0.978	3.02
Ni_3Sn_2	ord. hex., $InNi_2$ type ($B8_2$)	8.94	1.00	3.96
Pb_3Tl_5	disord. fcc (A1)	11.72	1.00	1.96
KNa_2	ord. fcc, Cu_2Mg type (C15)	0.98	1.03	3.01
NaPb	ord. bc tetragonal	5.97	1.03	4.22
$NaPb_3$	ord. cubic, $AuCu_3$ type ($L1_2$)	9.00	1.03	2.58
Hg_2K	ord. hex., AlB_2 type (C32)	7.66	1.04	3.18
AgMg	ord. cubic, CsCl type (B2)	5.91	1.05	4.39
$Na_{15}Pb_4$	ord. bcc, $Cu_{15}Si_4$ type ($D8_6$)	3.00	1.10	2.49

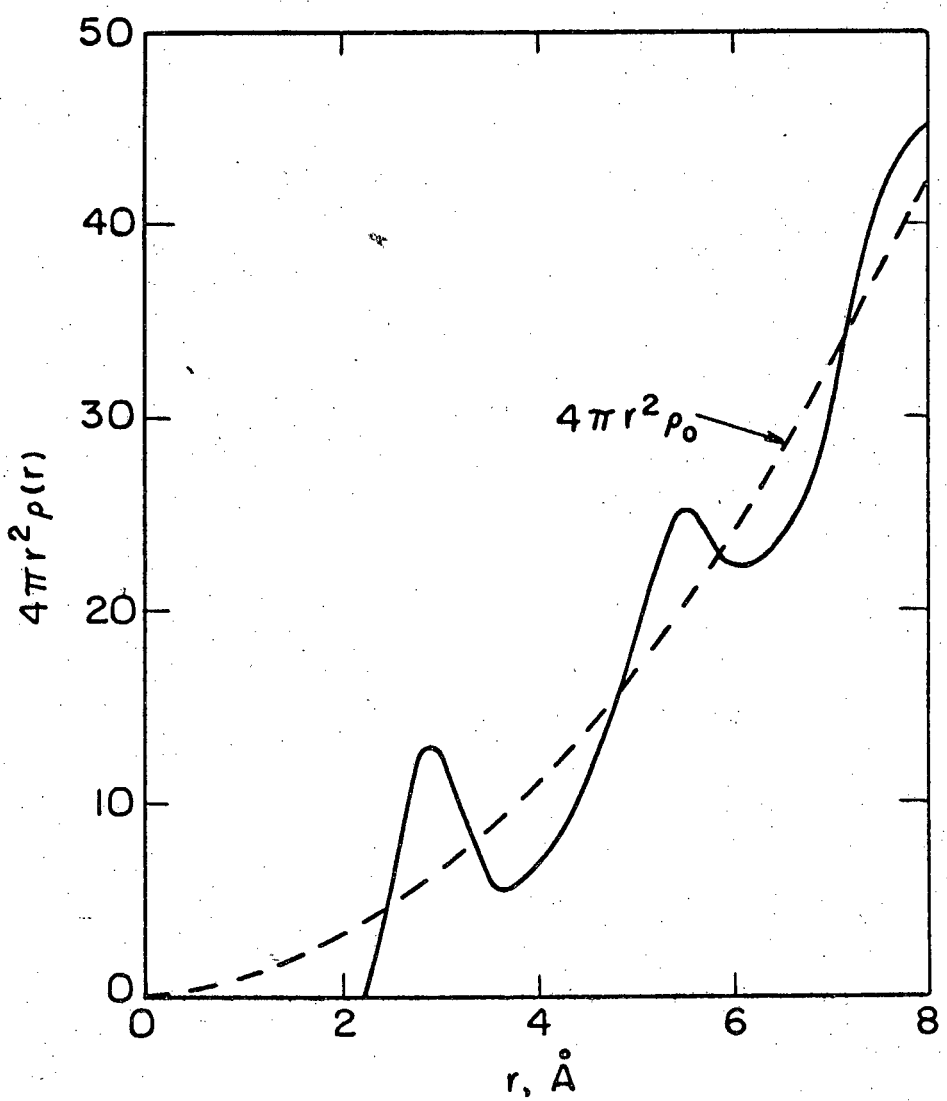

FIG. I ATOMIC DISTRIBUTION CURVE FOR LIQUID GOLD. (AFTER HENDUS[5])

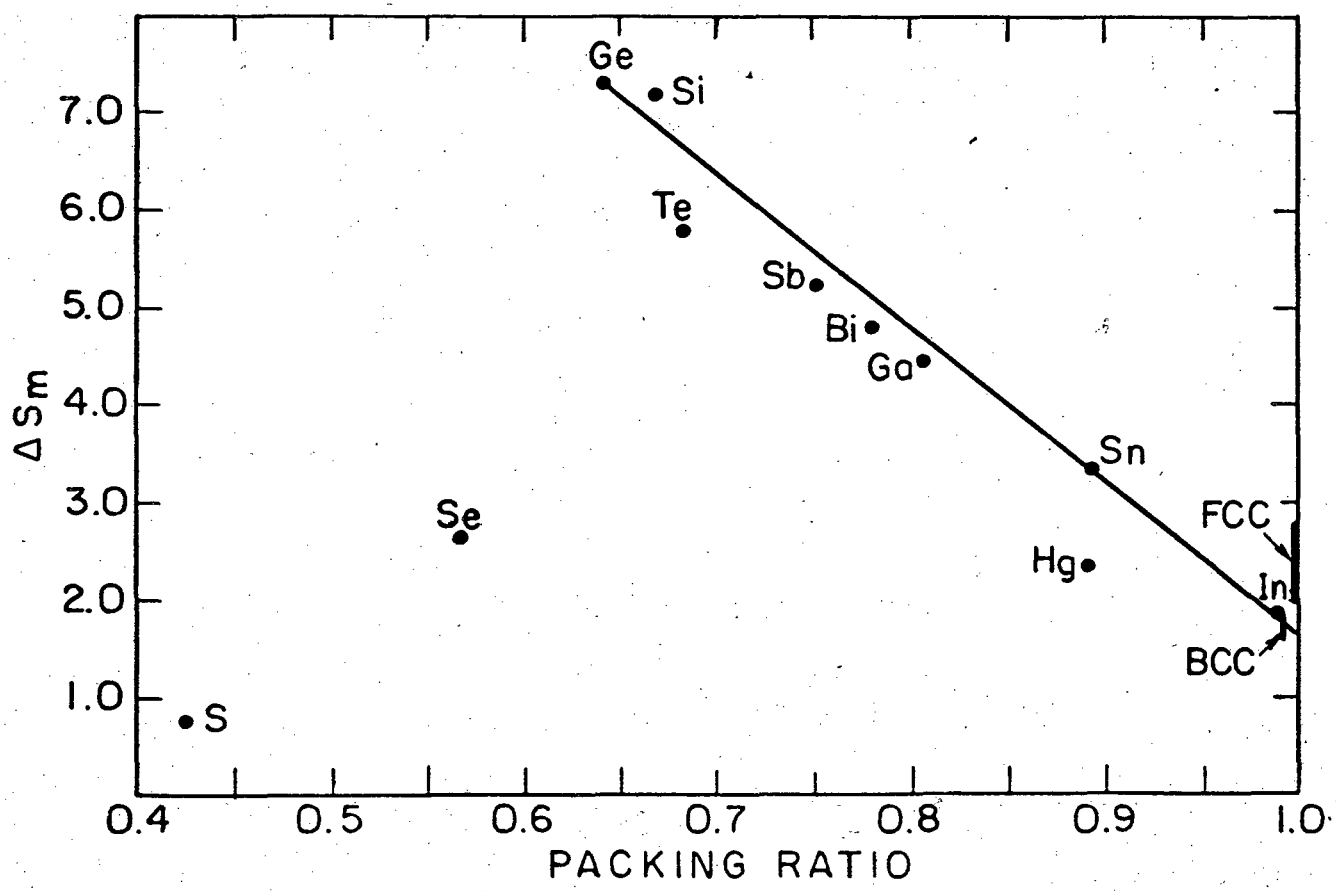

FIG. 2 ENTROPY OF MELTING vs. PACKING RATIO FOR ELEMENTS.

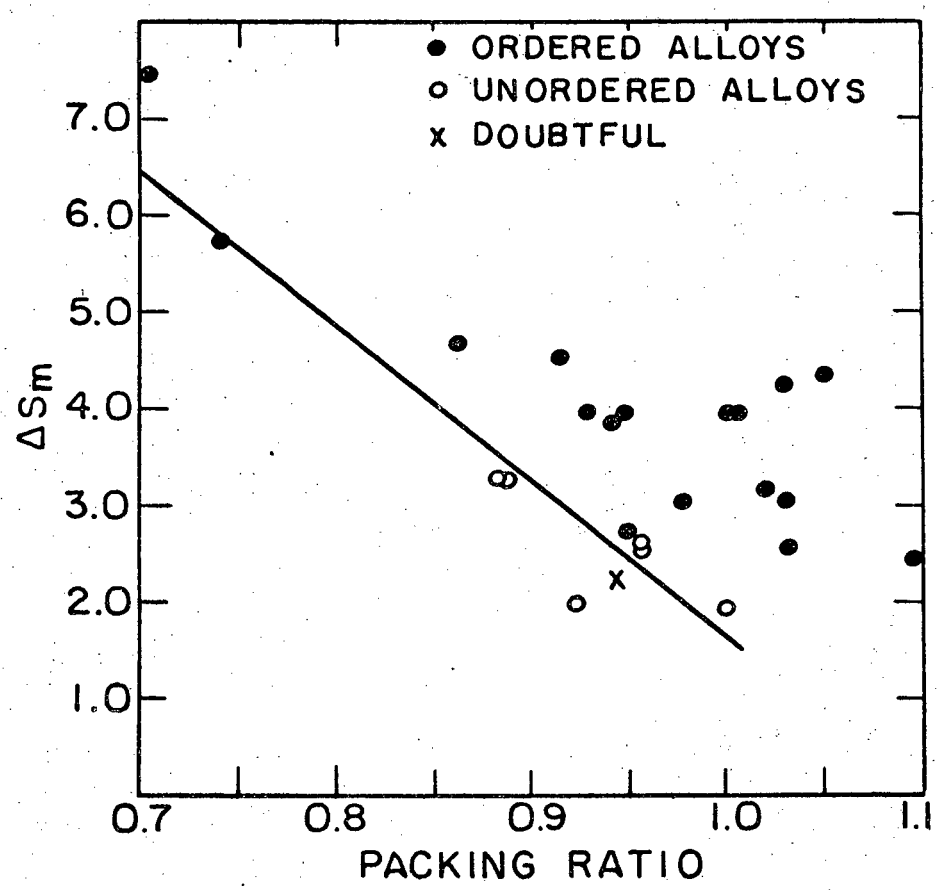

FIG. 3 ENTROPY OF MELTING vs. PACKING RATIO FOR ALLOYS. (SEE TABLE 3)

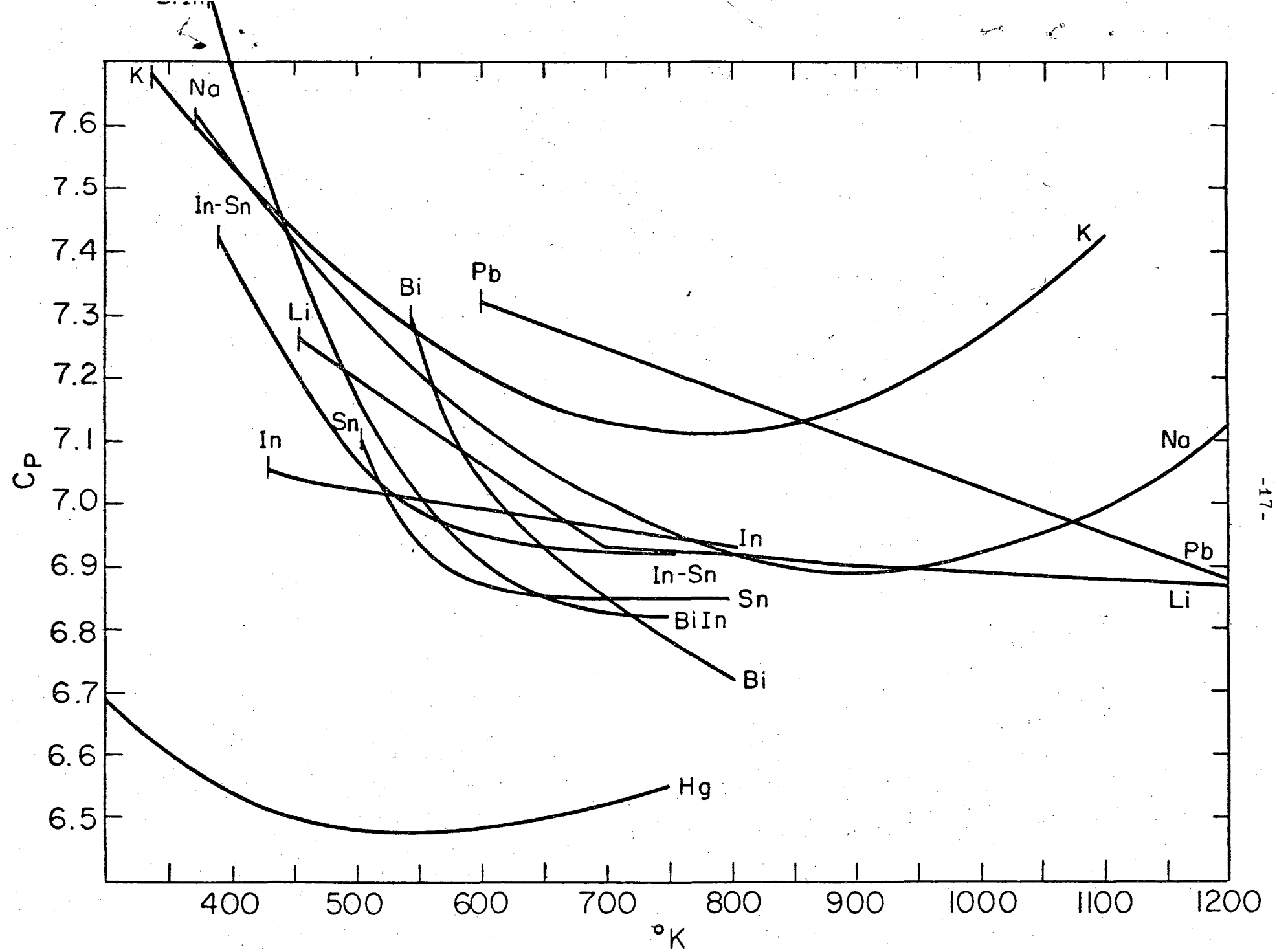

FIG. 4 AVAILABLE HEAT CAPACITY vs. TEMPERATURE DATA FOR LIQUID METALS AND ALLOYS.

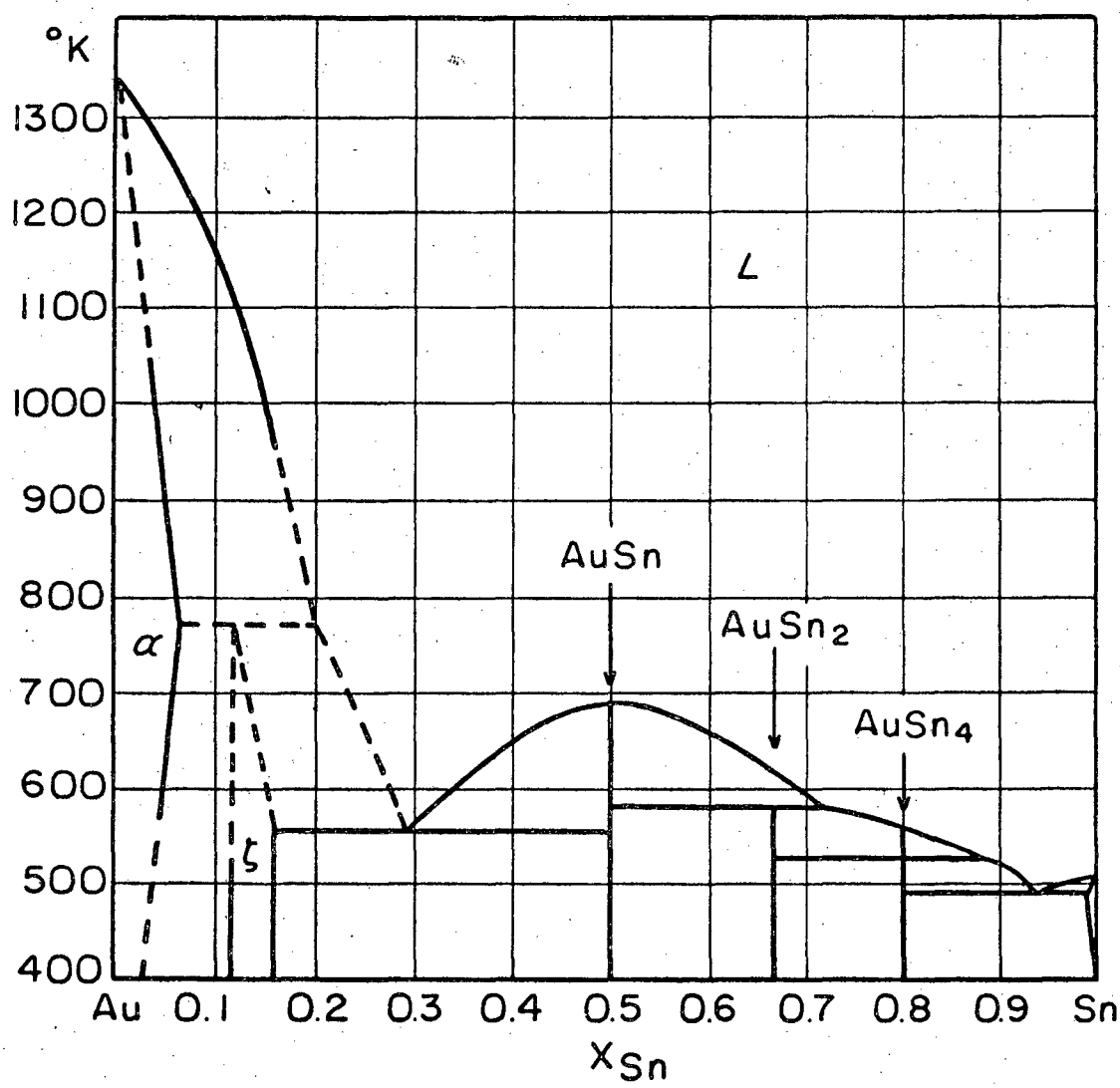

FIG. 5 PHASE DIAGRAM OF THE GOLD-TIN SYSTEM.

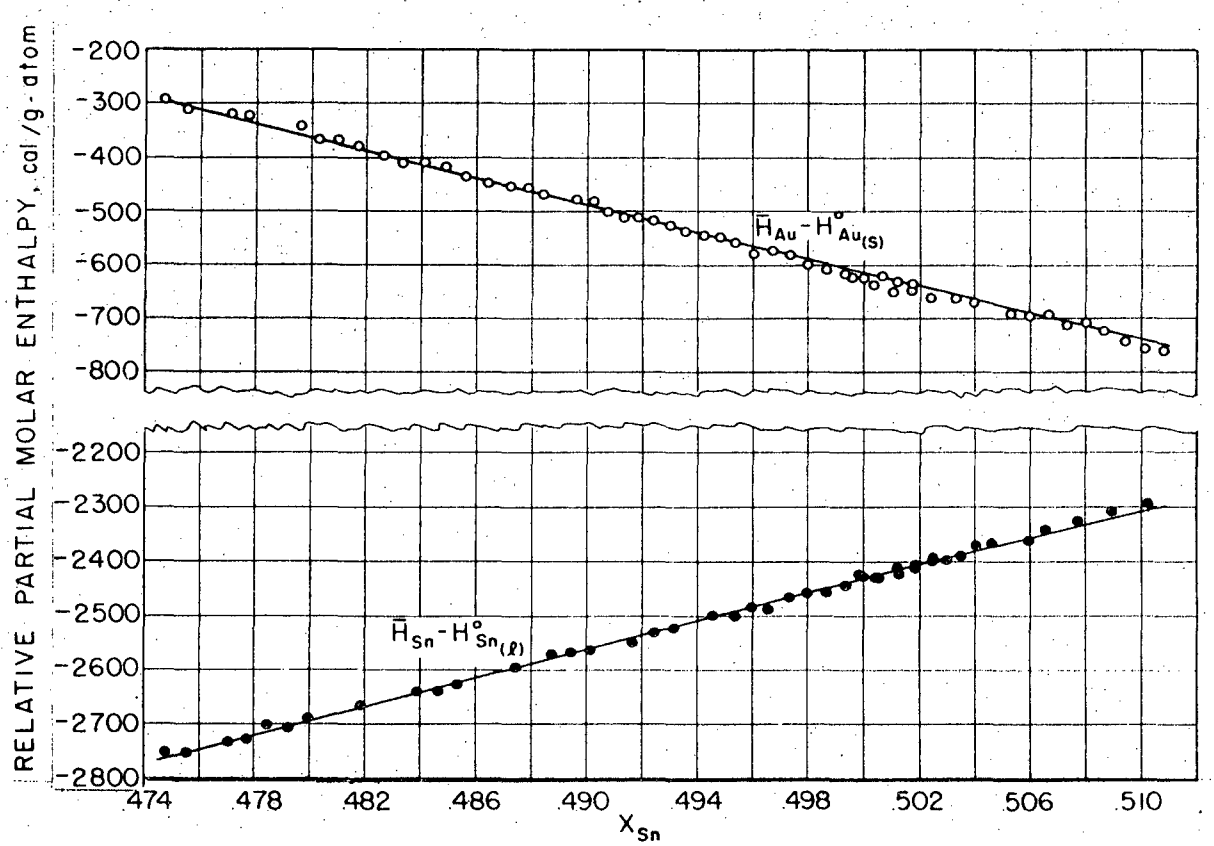

FIG. 6. RELATIVE PARTIAL MOLAR ENTHALPIES OF GOLD AND TIN IN LIQUID GOLD-TIN ALLOYS AT 696°K.

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