

On the Thermodynamic Properties of the Phases Zeta and AuSn in the System Au-Sn

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Metal solution calorimetry has been used to measure the low temperature heats of formation and heat contents of two phases in the system Au-Sn. The heats of formation of zeta containing 11.1, 14.0 and 16.0 at. pct Sn and AuSn at 78 K and of zeta containing 16.0 at. pct Sn and AuSn at 195 and 273 K have been measured. The heat contents ($H_{273\text{ K}} - H_{78\text{ K}}$) and ($H_{195\text{ K}} - H_{78\text{ K}}$) of zeta (16.0 at. pct Sn) and AuSn have also been measured. Heat contents at several temperatures and the standard heat and free energy of formation of AuSn at 298 K have been calculated. The stability of zeta and the unusual composition dependence of its heat of formation have been discussed in terms of its electronic structure.

VARIOUS physical and chemical properties of the Au-Sn system show unusual behavior at the gold rich end.¹⁻³ The alloy containing 25 at. pct Sn exhibits properties in the liquid state which are characteristic of structural complexity as in ordering or association in liquid alloys.^{2,3} When rapidly cooled, this alloy consists of a γ -brass type phase containing 20.5 at. pct Sn with a large negative heat of formation.⁴ The equilibrium phase at 20.5 at. pct Sn, however, is primarily zeta rather than γ , which is generally very stable. The available values of the heats of formation of zeta at 273 K⁵ appear to be too low compared with those at 723 K.⁶ Also the heats of formation of zeta at 273 K when plotted against its composition show an unusual negative curvature. This implies metastability of zeta, unless the entropy of formation makes an appreciable contribution to the free energy of formation at this temperature. It has been suggested that this behavior may be related to changes in the electronic structure of zeta.⁵ In zeta, the overlap of Fermi electrons across (10.0) faces of the Brillouin zone takes place at about 12 at. pct Sn.⁷ However, compared with the electronic effects, the temperature effects may be much larger at 273 K. At low temperatures, the temperature effects may be considerably reduced.

Measurement of accurate values of the heats of formation below room temperature is possible in principle by means of a metal solution calorimeter which is normally used to measure high temperature heats of formation and heats of solution.⁸ In this method, samples of an alloy and a mechanical mixture of its components having the same composition as the alloy are alternately added from a fixed addition temperature to a liquid metal solution bath and the heat effects on dissolution are measured. The difference in the heat effects due to the addition of the alloy and the corresponding mechanical mixture is the heat of formation of the alloy at the addition temperature. By maintaining the addition temperature below room temperature values of the heat of formation at low temperatures can be obtained.

In this investigation, metal solution calorimetry was

used to measure the heats of formation at temperatures as low as 78 K. The heats of formation of zeta containing 11.1, 14.0, and 16.0 at. pct Sn at 78 K and those of zeta containing 16.0 at. pct Sn at 195 and 273 K were measured. The heats of formation of the compound AuSn which appears next to zeta in the Au-Sn phase diagram were also measured at 78, 195, and 273 K. The heat contents ($H_{273\text{ K}} - H_{78\text{ K}}$) and ($H_{195\text{ K}} - H_{78\text{ K}}$) of zeta containing 16.0 at. pct Sn and of AuSn were measured. The heat contents at several temperatures below room temperature and the standard heat and free energy of formation at 298 K of AuSn were calculated. The stability of zeta and the unusual composition dependence of its heat of formation will be discussed.

EXPERIMENTAL

Samples of the phase zeta containing 11.1, 14.0, and 16.0 at. pct Sn and of AuSn were prepared by melting appropriate amounts of 99.999 wt pct Au and 99.99 wt pct Sn in evacuated and sealed Vycor tubes. The tubes containing the molten alloys were quenched in water. The resulting ingots were sealed in evacuated Vycor tubes and annealed for four weeks at 523 K. Metallographic and X-ray examination did not give any indication of segregation or the presence of a second phase.

The details of the tin solution calorimeter used in this investigation have been described elsewhere.⁸ For conducting an experiment a liquid tin rich bath was maintained in the calorimeter at 623 K. About 1.5 g of the sample were placed in the sample chamber; this chamber consisted of a 1 cm diam glass tube which was closed at one end and at the other end was connected to the calorimeter vessel through a ground glass joint. The sample tube was inserted in a constant temperature bath maintained in a dewar flask. In order to add the sample, the constant temperature bath was quickly removed and the specimen tube rotated around the ground glass joint. The constant temperature bath consisted of liquid nitrogen, dry ice and acetone or ice and water which yielded temperatures of 78, 195, and 273 K, respectively. The calorimeter was calibrated by adding tin from 273 K. The value of the heat content ($H_{623\text{ K}} - H_{273\text{ K}}$) of tin required⁹ for calculating the heat capacity of the calorimeter was taken as 4.079 kcal/g-atom (17.07 kJ/g-atom).⁹

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Table I. The Heat Effects of Additions to a Liquid Tin Rich Bath at Infinite Dilution and 623 K, the Heats of Formation, and the Heat Contents of the Phases AuSn and Zeta

Phase	Atom Fraction of Tin in Phase, X_{Sn}	Temperature, T , K	Heat Effect on Addition to Tin Rich Bath at Infinite Dilution and 623 K, $h_{x_{Au} \rightarrow 0}$		Heat of Formation at Addition Temperature ΔH_T		Heat Content, $(H_T - H_{78}K)$	
			kcal/g-atom	kJ/g-atom	kcal/g-atom	kJ/g-atom	kcal/g-atom	kJ/g-atom
AuSn	0.500	273	4.095 ± 0.030	17.14 ± 0.13	-3.610	-15.11	1.065	4.46
		195	4.540 ± 0.030	19.00 ± 0.12	-3.585	-15.01	0.620	2.60
		78	5.160 ± 0.050	21.60 ± 0.21	-3.555	-14.88	0	0
Zeta	0.160	273	-0.940 ± 0.010	-3.935 ± 0.042	-1.020	-4.27	1.015	4.249
		195	-0.435 ± 0.010	-1.821 ± 0.042	-1.060	-4.44	0.510	2.135
		78	+0.075 ± 0.025	+0.314 ± 0.105	-0.930	-3.89	0	0
	0.140	78	-0.245 ± 0.020	-1.026 ± 0.084	-0.755	-3.16	0	0
	0.111	78	-0.795 ± 0.015	-3.328 ± 0.063	-0.415	-1.74	0	0

In a calorimetric run, several consecutive additions of samples of the same phase were made. Several calibrating additions of tin were also made during each run. The heat effect resulting from the addition of a sample was determined and plotted against the atom fraction of gold in solution x_{Au} in the solvent bath. The atom fraction was taken as the average of the atom fractions of gold in solution before and after the addition of the sample.¹ The observed linear composition dependence of the heat effect was consistent with published values.¹ The heat effect at infinite dilution was obtained by extrapolation from such plots.

RESULTS AND DISCUSSION

The heat effect on addition of specimens of a phase from temperature T to tin rich solutions at infinite dilution at 623 K is:

$$\begin{aligned}
 h_{x_{Au} \rightarrow 0} \rightarrow 0 = & -\Delta H_T + X_{Au}(H_{623\text{K}} - H_T)_{Au} \\
 & + X_{Sn}(H_{623\text{K}} - H_T)_{Sn} \\
 & + X_{Au} \Delta \bar{H}_{Au}, x_{Sn} \rightarrow 1, 623\text{K}
 \end{aligned} \quad [1]$$

where h = heat effect per g-atom of the addition, ΔH_T = heat of formation of the phase at T K, x_i = atom fraction of component i in the tin rich solution, X_j = atom fraction of component j in the phase, $\Delta \bar{H}_{Au}$ = partial g-atomic enthalpy of gold relative to solid gold. The heat effects of addition at infinite dilution of various phases added from different temperatures are listed in Table I. The heat contents ($H_{623\text{K}} - H_{78\text{K}}$), ($H_{623\text{K}} - H_{195\text{K}}$), and ($H_{623\text{K}} - H_{273\text{K}}$) were taken from the literature⁹ as 5.224, 4.563 and 4.079 kcal/g-atom (21.87, 19.10, and 17.07 kJ/g-atom), respectively, for tin and as 3.275, 2.636 and 2.175 kcal/g-atom (13.71, 11.03, and 9.10 kJ/g-atom), respectively, for gold. A measured value for $\Delta \bar{H}_{Au}, x_{Sn} \rightarrow 1$ at 623 K is -5.286 kcal/g-atom (-22.13 kJ/g-atom).¹ Values of the heats of formation ΔH_T obtained by substituting these data into Eq. [1] are listed in Table I.

As shown by Eq. [1], the difference between the heat effects of a phase added from two different temperatures is the difference between its heat contents at the addition temperatures. Heat contents determined in this manner are listed in Table I.

The random errors calculated as the root-mean-square average scatter in the heat effects are included in Table I. The uncertainty limits in ΔH are the same as those in the corresponding heat effects and the uncertainties in $(H_T - H_{78})$ are ± 50 cal/g-atom (± 210 J/g-atom) in the heat contents of AuSn and ± 25 cal/g-atom (± 105 J/g-atom) in the heat contents of zeta (16 at. pct Sn). The results are also affected by systematic errors arising from uncertainties in the heat contents of gold and tin⁹ and the partial g-atomic enthalpy of gold in tin at 623 K.¹ The systematic errors are estimated to be about ± 10 cal/g-atom (± 42 J/g-atom) in the heat effects of additions and ± 20 to 25 cal/g-atom (± 84 to 105 J/g-atom) in the heats of formation and heat contents.

Heat Content of AuSn

The heat contents of AuSn below room temperature are not available, but those at high temperatures have been measured.^{10,10a} In order to test the consistency of the heat contents for high temperatures with those for low temperatures and to select heat contents for other temperatures, the following procedure was adopted.

Assuming a single valued average Debye temperature, negligible anharmonic and magnetic contributions and constancy of the Grüneisen parameter the heat content H_T at any temperature T may be written as:¹¹

$$(H_T - H_0) = U(\Theta/T) + \phi + (1/2)\gamma_e T^2 \quad [2]$$

where $U(\Theta/T)$ = Debye internal energy corresponding to an average Debye temperature Θ , $\phi = \int_0^T \gamma \alpha C_v T dT$, γ = Grüneisen constant, α = volume coefficient of expansion, C_v = heat capacity at constant volume and γ_e = the constant term in the electronic heat capacity. For evaluating the function ϕ , C_v has been assumed to equal¹² $3R/[1 + (1/20)(\Theta/T)^2]$, and α is expressed as¹³ $A/[1 + (1/20)(\Theta/T)^2]$, where A is a constant. It may be shown that:

$$\begin{aligned}
 \phi = & 1.5R A \gamma \theta^2 \{ (T/\theta)^2 + (T/\theta)^2 / [20(T/\theta)^2 + 1] \\
 & - 0.1 \ln [20(T/\theta)^2 + 1] \}
 \end{aligned} \quad [3]$$

The heat contents of AuSn below room temperature measured in this investigation and those reported for AuSn above room temperature¹⁰ are well represented to within ± 7 cal by Eq. [2] when $\theta = 225$ K, $A\gamma = 1.65$

Table II. Heat Content of AuSn Calculated by Eq. [2] from Published Data and Data Measured in This Investigation

Temperature, K	100	150	200	250	298	400	500	600
$(H_T - H_0)$, kcal/g-atom	0.24	0.50	0.78	1.08	1.37	2.01	2.65	3.31
$(H_T - H_0)$, kJ/g-atom	1.00	2.09	3.27	4.52	5.73	8.41	11.09	13.86

$\times 10^{-4} \text{ deg}^{-1}$ and $\gamma_e = 2.5 \times 10^{-4} \text{ cal/g-atom-K}$ ($10.5 \times 10^{-4} \text{ J/g-atom-K}$). This value of γ_e agrees well with that estimated from the carrier concentration.¹⁴ No published value for the Debye temperature of this compound is available for comparison. The determined value of $A\gamma$ agrees well with a value of approximately $1 \times 10^{-4} \text{ deg}^{-1}$ found for a number of phases.¹⁵ Heat contents of AuSn calculated by Eq. [2] for several temperatures are listed in Table II.

The Standard Heat and Free Energy of Formation of AuSn

A heat of formation of $-3.645 \text{ kcal/g-atom}$ (-15.26 kJ/g-atom) has been reported for AuSn at 273 K.⁵ This result was obtained by tin solution calorimetry using an older value for the heat content of tin.⁵ When more recent values for the heat content⁹ are combined with the earlier measured values, the heat of formation becomes $-3.59 \pm 0.045 \text{ kcal/g-atom}$ ($-15.03 \pm 0.19 \text{ kJ/g-atom}$) in good agreement with the value of $-3.61 \pm 0.03 \text{ kcal/g-atom}$ ($-15.11 \pm 0.13 \text{ kJ/g-atom}$) reported here.

The heat of formation at any temperature T may be expressed as:

$$\Delta H_T = \Delta H_0 + (H_T - H_0)_p - \sum_j X_j (H_T - H_0)_j \quad [4]$$

where the subscripts p and j indicate the phase and its components respectively. From the measured heats of formation (Table I), the heat contents of AuSn (Table II) and the published heat contents of gold and tin,⁹ a value of $-3.505 \text{ kcal/g-atom}$ (-14.67 kJ/g-atom) was obtained for ΔH_0 . ΔH_{298}^0 is found by Eq. [4] to be $-3.605 \text{ kcal/g-atom}$ (-15.09 kJ/g-atom).

The free energy of formation ΔG at any temperature T may be written as:

$$\Delta G_T = \Delta H_0 + (G_T - H_0)_p - \sum_j X_j (G_T - H_0)_j \quad [5]$$

The quantity $(G_T - H_0)$ for AuSn may be found from the following expression:¹¹

$$(G_T - H_0) = F(\theta/T) + \phi - T\psi - (1/2)\gamma_e T^2 - TS_0 \quad [6]$$

where $F(\theta/T)$ = Debye free energy, S_0 = entropy at 0 K, and:

$$\begin{aligned} \psi &= \int_0^T \gamma \alpha C_v dT \\ &= A\gamma U(\theta/T) + 0.268 R\gamma A\theta \tan^{-1}(\sqrt{20} T/\theta) \\ &\quad + 0.15 R\gamma A\theta [(T/\theta)/\{20(T/\theta)^2 + 1\}] \end{aligned} \quad [7]$$

Equations [5] to [7] are evaluated from published free energies of gold and tin⁹ and values of θ , $A\gamma$, γ_e , and ΔH_0 as found above and by assuming S_0 to be zero for AuSn. The value obtained for ΔG_{298}^0 is -3.075

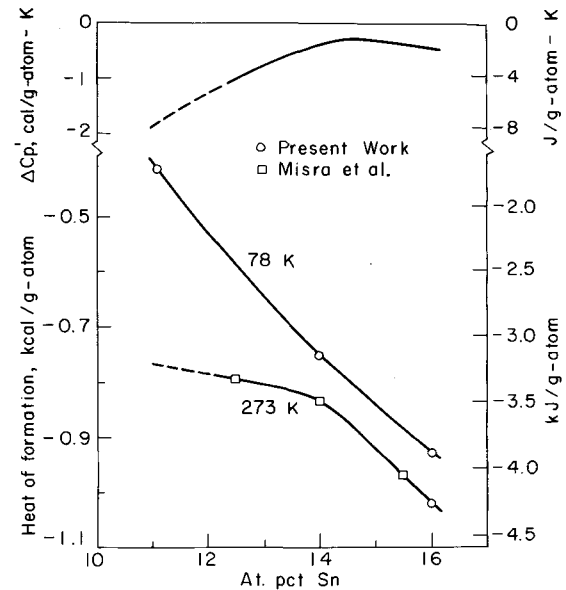


Fig. 1—Heats of formation and average relative heat capacity ΔC_p of zeta as functions of composition.

kcal/g-atom (-12.87 kJ/g-atom). No experimental values of the free energy of formation are available for comparison.

Heat of Formation of Zeta

The heats of formation at 273 K of three compositions of the zeta phase have been reported.⁵ As stated above, these data were determined with an older value of the heat content of tin. Corrected data, together with the results obtained in the present investigation, are plotted against composition in Fig. 1. The two sets of data are consistent with each other.

Stability of Zeta

Figure 1 shows that the unusual negative curvature of the heat of formation *vs* composition curve at 273 K has completely disappeared at 78 K. At this temperature the heat of formation *vs* composition curve has the normal positive curvature. The free energy of formation of zeta at 78 K can be calculated from its heats of formation and the entropy of mixing of a disordered structure¹⁶ neglecting the contribution of the excess entropy at this temperature. The free

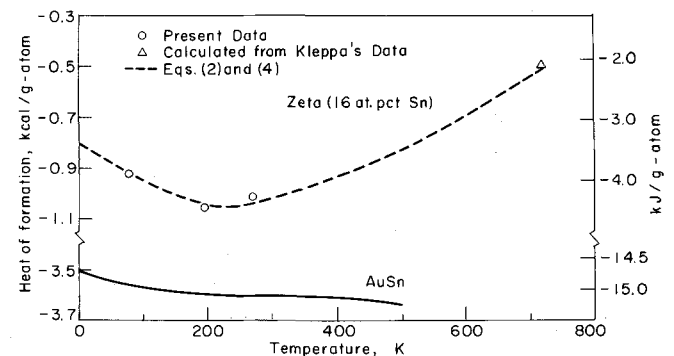


Fig. 2—Heats of formation of zeta containing 16 at. pct Sn and AuSn relative to solid gold and solid tin as functions of temperature. See text for explanation.

energy of formation against composition curve of zeta is concave towards the composition axis and is consistent with the stability of zeta over the composition range of 11 to 16 at. pct Sn. Any effect of the change in the electronic structure of zeta on ΔH is not detectable at 78 K. However the free energy of formation of zeta at 273 K calculated from its heats of formation and the ideal entropy of mixing is convex towards the composition axis and is inconsistent with the observed stability of zeta. It implies that the temperature effects due to excess entropy are appreciable at 273 K.

The heats of formation of zeta containing 16 at. pct Sn are plotted against temperature in Fig. 2. Those of AuSn are also shown for comparison. These are obtained by substituting the values of ΔH_o and the heat contents of AuSn (Table II), gold⁹ and tin⁹ in Eq. [4]. The heats of formation of AuSn decrease continuously with increase in temperature whereas those of zeta decrease only up to about 200 K and increase above this temperature. Thus above room temperature the heat of formation is expected to be very small. Kleppa⁶ measured the heats of formation of zeta containing 13 at. pct Sn and AuSn at 723 and 623 K, respectively. He has reported that his results contain appreciable systematic errors caused by his electrical calibration system.¹⁷ Comparison of his value of ΔH of AuSn at 623 K with that obtained from the present data yields a systematic error of 5.53 pct. Kleppa's corrected value for the heat of formation relative to solid gold and solid tin is -0.28 kcal/g-atom (-1.17 kJ/g-atom) at 723 K for zeta containing 13 at. pct Sn. Assuming the composition dependence of the heat of formation between 13 and 16 at. pct to be approximately the same at 273 and 723 K, the heat of formation of zeta containing 16 at. pct Sn is only -0.495 kcal/g-atom (-2.07 kJ/g-atom) at 723 K relative to solid gold and solid tin. This is much smaller in magnitude compared with the corresponding value of -1.02 kcal/g-atom (-4.27 kJ/g-atom) measured in this investigation at 273 K. Kleppa's results thus confirm the observed tendency of the heats of formation to increase with temperature.

A negative heat of formation of a compound suggests that the bonds in the compound are relatively stronger than those in the components. Stronger bonds are characterized by higher frequencies of vibration of the lattice and higher Debye temperatures. The contribution of the lattice heat capacities to ΔC_p , therefore, is negative. Since near 78 K all other contributions to ΔC_p are usually small compared with that of the lattice, the temperature dependence of ΔH would have an appreciable negative value. With increasing temperature the difference between the lattice heat capacities becomes small and other terms become increasingly important, so that the magnitude of the temperature dependence of ΔH would tend to decrease with increase in temperature. Various phases^{11,18,19} including AuSn (Fig. 2) behave in this manner.

The heat capacity difference ΔC_p of AuSn is negative and its magnitude decreases slightly with increasing temperature. Zeta behaves like this only at low temperatures. The value of ΔC_p is negative below 200 K. Above this temperature it is positive and suggests that there is a strong positive contribution to the heat content of zeta (16 at. pct Sn) at high temperature. A positive contribution to the heat content

arises from the thermal excitation of electrons. The Fermi surface in the zeta phase rich in gold already touches the {10.0} and {00.2} faces of the Brillouin zone.^{7,20} With increasing tin content the electron to atom ratio increases and at about 12 at. pct Sn the Fermi surface overlaps the {10.0} faces of the Brillouin zone. A value of γ_e estimated¹⁴ for the 16 at. pct Sn alloy is only 1.8×10^{-4} cal/g-atom-K² (7.5×10^{-4} J/g-atom-K²). This term cannot be responsible for the large positive contribution to ΔH .

The values of the heats of formation of zeta containing 16 at. pct Sn measured in this investigation at 78, 195, and 273 K and calculated from Kleppa's data at 723 K and the value of γ_e stated above, when substituted in Eqs. [2] and [4] yield average values of 351 K for θ and 6×10^{-4} deg⁻¹ for $A\gamma$. The experimental values and those calculated from Eqs. [2] and [4] are shown in Fig. 2 to be in good agreement. The value of $A\gamma$ obtained from these equations is unusually large. Because of this large dilatational term the excess entropy is large and zeta is more stable than the γ -phase.

The quantity $\Delta C'_p = (\Delta H_{273\text{K}} - \Delta H_{78\text{K}})/195$ of the zeta phase are shown in Fig. 1 as a function of its composition. The value of $\Delta C'_p$ at the gold rich end is comparable with the low temperature relative heat capacity of the tin rich zeta phase containing 16 at. pct Sn (Fig. 2), but with increasing tin content $\Delta C'_p$ increases due to the increasing positive contribution from the dilatational term. The variation of $\Delta C'_p$ with composition suggests that the dilatational contribution increases rapidly with increasing tin content, is maximum at about 14.5 at. pct Sn and decreases slightly beyond this composition. The deviation of the c/a ratio of the zeta phase from the ideal value also changes in this manner and the ideal c/a ratio occurs at 14.5 at. pct Sn.¹⁶ The increasing dilatational contribution with increasing tin content and the large dilatational contribution in the tin rich zeta are probably due to the changes in the axial ratios of the zeta phase with composition resulting from the interaction of the Fermi surface with various faces of the Brillouin zone.^{7,20}

SUMMARY AND CONCLUSIONS

1) The heats of formation of the phase zeta containing 16.0 at. pct Sn and of AuSn have been measured at 78, 195, and 273 K. The heats of formation of zeta containing 11.1 and 14.0 at. pct Sn at 78 K have also been measured (Table I).

2) The heat contents ($H_{273\text{K}} - H_{78\text{K}}$) and ($H_{195\text{K}} - H_{78\text{K}}$) of the zeta phase containing 16.0 at. pct Sn and of AuSn have been measured (Table I).

3) The heat contents of AuSn at several temperatures (Table II) and the standard heat and free energy of formation of AuSn have been calculated. The heat of formation changes with temperature in the normal manner.

4) The curves showing the change of ΔH of zeta with composition have the usual positive curvature at 78 K, but a very unusual negative curvature at 273 K (Fig. 1). The temperature dependence of ΔH also changes appreciably with composition.

5) As shown by the heats of formation (Fig. 2), ΔC_p of zeta containing 16 at. pct changes from negative below about 200 K to positive at higher temperatures.

This behavior is attributed to a large dilatational contribution to the heat content of zeta rich in tin. It is suggested that the dilatational contribution is related to the variation of the axial ratio of zeta with composition due to the interaction of the Fermi surface with the faces of the Brillouin zone.

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