International Journal of Thermophysics, Vol. 16, No. 3, 1995

An Analysis of the Specific Heat Capacity of Liquid Au–Sn Alloy Based on the Ideal-Associated Solution Model[1]

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The specific heat capacity of Au–Sn liquid alloy was analyzed using the ideal associated solution model assuming associated compounds Au_3Sn, AuSn, and $AuSn_2$. Based on this model, all of the specific heat capacity, heat of mixing, and activity are described over a wide temperature range. Further, it became clear that the summation of mole numbers of the species in the liquid alloy shows a minium at the stoichiometric composition of Au_3Sn, which implies that the liquid is the most ordered at this composition.

KEY WORDS: activity; associated compounds; Au–Sn liquid alloy; heat of dissociation; heat of mixing; ideal associated solution; specific heat capacity.

1. INTRODUCTION

Many papers concerning various fields of research of liquid alloys have described the possible existence of associated compounds (AC) consisting of the component elements of the alloys [1–13]. Some of the peculiarities often observed in the concentration dependence of the thermodynamic and physical quantities (large negative values of heat of mixing, activity deviated strong-negatively, the peaks of electric resistance and viscosity, etc.) are probably the evidence of AC. Nowadays some liquid models assuming AC are presented for describing the thermodynamic properties of

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[1] Paper presented at the Twelfth Symposium on Thermophysical Properties, June 19–24, 1994, Boulder, Colorado, U.S.A.

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these alloys [1-5]. Each model seems to succeed in describing activities, heat of mixing, and liquidus of the phase diagrams. However, many parameters of interaction between species being introduced in these models, the calculation is complex. Therefore they can assume only one or two AC. From a viewpoint of existence of plural solid compounds in many alloy systems, and also judging from observed peculiarities, it needs to consider plural AC. If it is easy to take plural AC into account, application to much more liquid systems and total discussion of the existence and properties of AC will become possible. Recently, we reported that the ideal associated solution model assuming plural AC is effective for describing all of the activities, heat of mixing, and specific heat capacity and their temperature dependence [8-13]. Based on this model we report here the detailed results of analysis of the Au-Sn liquid system.

Concerning the Au-Sn liquid system, some peculiarities are reported, but the reports contradict each other regarding the composition where the peculiarities are observed. The electrical resistance shows a large peak near 75 at% Au [14, 15], and the excess integral entropy has a minimum at the same composition [16], implying the existence of Au_3Sn, while the excess integral entropy also has a minimum at 45 at% Au [16], and the heat of mixing has a minimum at 65-50 at% Au [17], which probably indicates the coexistence of AuSn. However, the specific heat capacity has no peak at 75 at% Au, though it has a peak at 50 at% Au and a shoulder near 30 at% Au [18]. Also, there is a discrepancy in interpretation of X-ray measurements; one suggests the existence of Au_3Sn and the other suggests AuSn [19, 20]. In the phase diagram, the solid compounds AuSn, $AuSn_2$, and $AuSn_4$ are found but there is no solid compound Au_3Sn. Therefore, this report contains not only an explanation of the specific heat capacity of the Au-Sn liquid system by this model but also the elucidation of these discrepancies mentioned above.

2. THEORY AND ANALYSIS

2.1. Theory

The specific heat capacity of Au-Sn liquid alloy at constant pressure (C_p^l) is expressed by the following equations assuming Au_3Sn, AuSn, and $AuSn_2$ as AC which are represented generally by the chemical formula $Au_{p_i}Sn_{q_i}$ [13]. The subscript and superscript i are the number given to each species (1 = Au, 2 = Sn, 3 = Au_3Sn, 4 = AuSn, 5 = $AuSn_2$): x_i, C_p^i, ΔH_i^0, and T are the molar fraction, the molar specific heat capacity of the ith species at constant pressure, the standard enthalpy of formation of AC, and the temperature, respectively.

$$C^{l}_{p} = \left(\sum_{i} x_i C^{i}_{p}\right)\Big/ X_S + \left\{\sum_{i \neq 1,2} \Delta H^0_i (\partial x^*_i/\partial T)\right\}\Big/ X_S \tag{1}$$

$$\partial x^*_i/\partial T = -\left(x_i \Big/ \sum_k p_k x_k\right) \sum_k (p_k\, \partial x_k/\partial T) + \partial x_i/\partial T \tag{2}$$

$$X_S = \sum_i (p_i + q_i)\, x_i = (x_1 + x_2 + 4x_3 + 2x_4 + 3x_5) \tag{3}$$

As clearly seen from Eqs. (1) and (2), the second term on the right-hand side of Eq. (1) shows the effect of the heat of dissociation of AC to C^l_p, while the first term shows the additivity of the molar specific heat capacity (Neumann–Kopp's rule). The $\partial x_i/\partial T$ in Eq. (2) can be expressed by x_i and ΔH^0_i [13]: x_i and ΔH^0_i can be calculated from the experimental values of the activities of Au and Sn (a_{Au}, a_{Sn}) and heat of mixing (ΔH^0_m) using the following equations [8]:

$$a_{Au} = x_1, \qquad a_{Sn} = x_2 \qquad a_i (i \neq 1, 2) = K_i a^{p_i}_{Au} a^{q_i}_{Sn} = x_i \tag{4}$$

$$\sum_i x_i = 1, \qquad X_{Sn} = \left(\sum_i q_i x_i\right)\Big/ X_S = N_B/(N_A + N_B) \tag{5}$$

$$\Delta H^0_m = (x_3\, \Delta H^0_3 + x_4\, \Delta H^0_4 + x_5\, \Delta H^0_5)/X_S \tag{6}$$

where a_i, K_i, and X_{Sn} are the activity of species i, the equilibrium constant of formation of AC, and the Sn concentration of this alloy, respectively. N_A and N_B are the mole numbers of elements Au and Sn of this alloy.

2.2. Analysis

The data used in this analysis are the C^l_p at 550–900 K measured by Janitsch et al. [18], the a_{Au} and a_{Sn} at 823 K reported by Hultgren et al. [21], the ΔH^0_m at 803 K measured calorimetrically by Hayer et al. [17], and the following C^1_p and C^2_p ($J \cdot mol^{-1} \cdot K^{-1}$):

in the range 1336.15–1600 K [22],

$$C^1_p = 50.252 - 1.2636 \times 10^{-2} T \tag{7}$$

and in the range 550–900 K [18],

$$C^2_p = 35.159 - 1.7414 \times 10^{-2} T + 1.0006 \times 10^{-5} T^2 \tag{8}$$

Equation (7), which was evaluated from the data above the melting point of Au reported by Hultgren et al. [22], was still used in the supercooled liquid region of Au at 550–900 K. Since mixing enthalpies measured by Hayer et al. [17] are the converted data for the standard state of Au from solid to liquid using $C_p^l = 30.960$, we recalculated them using Eq. (7).

This analysis was done by the use of a computer. Figure 1 shows the flowchart of this calculation. In this flowchart, n and the subscript n mean the number of repetitions of the calculation and the resultant values from this nth calculation. The ΔS_i^0 $(= R \ln K_i + \Delta H_i^0/T)$ is the standard entropy of formation of AC. By this process, C_p^l, a_{Au}, a_{Sn}, ΔH_m^0, and ΔS_i^0 at 550–900 K, which are all dependent in temperature can be obtained.

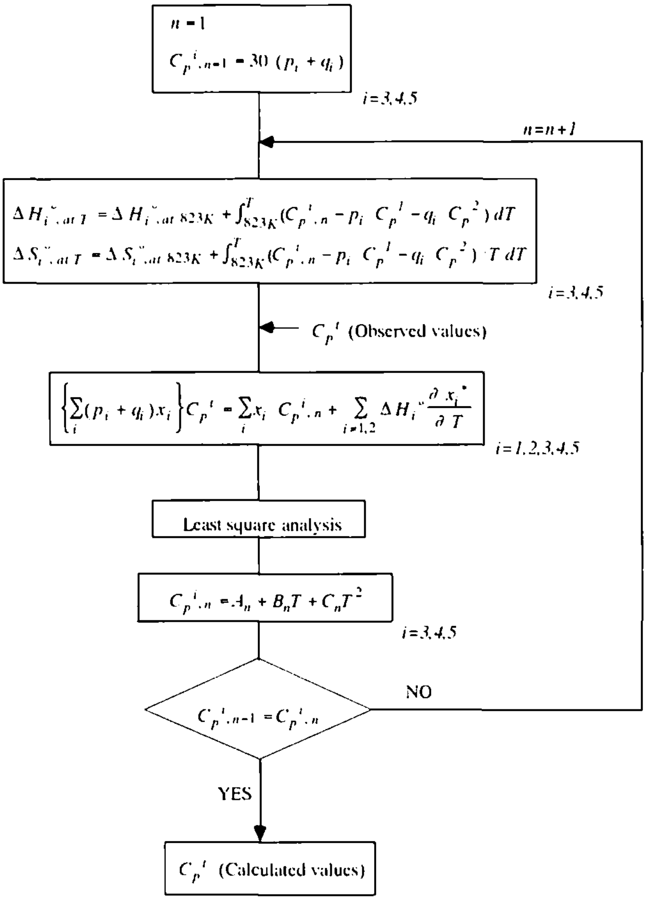

Fig. 1. Flowchart showing the method of calculation of the specific heat capacity of the liquid Au–Sn system.

2.3. Associated Compounds (AC)

We took into account Au_3Sn, AuSn, and $AuSn_2$ as AC. If Au_3Sn is not taken into account, K_5 becomes negative in spite of the restriction that K_i values should be all positive. This means that without Au_3Sn, the thermodynamic properties of the liquid cannot be explained. We omitted $AuSn_4$ from AC because its concentration is not so high that it has any effect on $a_{\rm Au}$, $a_{\rm Sn}$ at 823 K, and adequate $\Delta H^0_{\rm AuSn_4}$ and $C_{\rm p}^{\rm AuSn_4}$ cannot be obtained.

3. RESULTS AND DISCUSSION

The followings are the calculated values of ΔH^0_i and ΔS^0_i at 823 K.

$$\Delta H^0_3 \text{ at } 823\text{ K} = -34{,}859, \qquad \Delta S^0_3 \text{ at } 823\text{ K} = 25.192 \tag{9}$$

$$\Delta H^0_4 \text{ at } 823\text{ K} = -22{,}869, \qquad \Delta S^0_4 \text{ at } 823\text{ K} = 11.973 \tag{10}$$

$$\Delta H^0_5 \text{ at } 823\text{ K} = -40{,}879, \qquad \Delta S^0_5 \text{ at } 823\text{ K} = -16.911 \tag{11}$$

where ΔH^0_i is in $\rm J \cdot mol^{-1}$ and ΔS^0_i is in $\rm J \cdot mol^{-1} \cdot K^{-1}$. $C^3_{\rm p}$, $C^4_{\rm p}$, and $C^5_{\rm p}$ calculated as a function of T are written as follows:

$$C^3_{\rm p} = 180.43 - 1.1695 \times 10^{-1} T + 5.1540 \times 10^{-5} T^2 \tag{12}$$

$$C^4_{\rm p} = 175.22 - 2.4503 \times 10^{-1} T + 1.2661 \times 10^{-4} T^2 \tag{13}$$

$$C^5_{\rm p} = 190.50 - 2.6742 \times 10^{-1} T + 1.5329 \times 10^{-4} T^2 \tag{14}$$

where $C^i_{\rm p}$ is in $\rm J \cdot mol^{-1} \cdot K^{-1}$ and T is in K. The values of $C^{\rm l}_{\rm p}$, $a_{\rm Au}$, $a_{\rm Sn}$, and $\Delta H^0_{\rm m}$ calculated from Eqs. (9)–(14) are in good agreement with the experimental values [17, 18, 21, 23–25]. These results are shown in Figs. 2–4. The activity shown in Fig. 3 deviates more negatively at lower temperatures, and this deviation is somewhat large in the poor Sn region. Also, in Fig. 4, $-\Delta H^0_{\rm m}$ is a little larger in this Sn-poor region compared with that in the Sn-rich region. These facts suggest the existence of Au_3Sn. On the contrary, in Fig. 2, the $C^{\rm l}_{\rm p}$ curve shows a minimum in this region, though it surely represents a peak and a shoulder near the stoichiometric composition of AuSn and $AuSn_2$. It is partly because $\partial x_3/\partial T$ and $\partial x_4/\partial T$ have opposite signs in this region, thus it leads to a positive value of $\Delta H^0_3(\partial x^*_3/\partial T)$, a negative value of $\Delta H^0_4(\partial x^*_4/\partial T)$, and the cancellation of the each effect [cf. Eq. (2)]. In short, it happens because, when the temperature rises, Au_3Sn dissociates and the dissociated atoms form AuSn following the mass action law. In Fig. 5, $C^{\rm l}_{\rm p}$ at 700 K is shown with the calculated result of the first term of Eq. (1) ($= \sum_i x_i C^i_{\rm p}/X_s = A$) and, also, each second term due to the heat of dissociation of Au_3Sn, AuSn, and

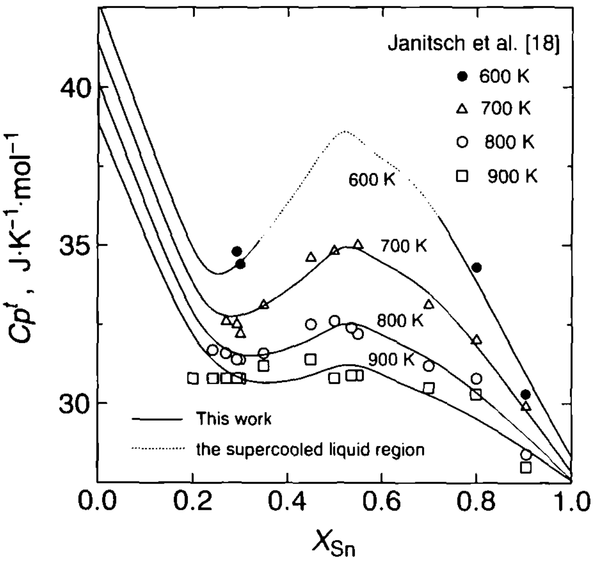

Fig. 2. The calculated C_p^l curves of the Au-Sn system at various temperatures.

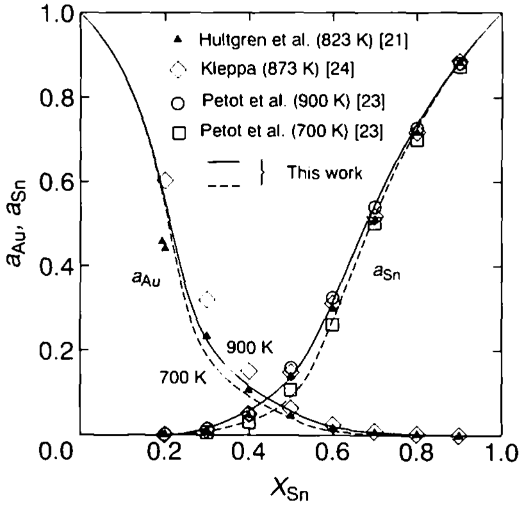

Fig. 3. The calculated activity curves a_{Au} and a_{Sn} at 900 and 700 K.

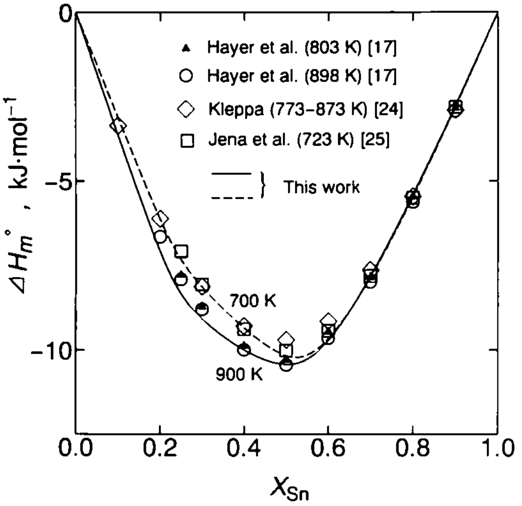

Fig. 4. The calculated mixing enthalpy curves ΔH_m^0 at 900 and 700 K.

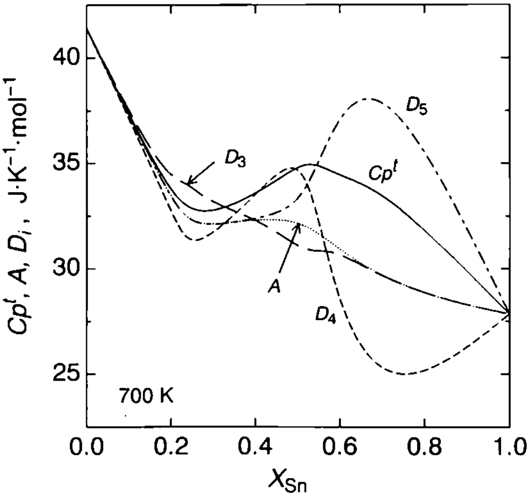

Fig. 5. The calculated C_p^l curves at 700 K, the additive part of C_p', and each contribution of the heat of dissociation of associated compounds. (····) $A = \sum_i x_i C_p'/X_S$; (– – – –) $D_3 = A + \Delta H_3^0(\partial x_3^*/\partial T)/X_S$; (- - - - - - -) $D_4 = A + \Delta H_4^0(\partial x_4^*/\partial T)/X_S$; (·-·-·-·-·) $D_5 = A + \Delta H_5^0(\partial x_5^*/\partial T)/X_S$.

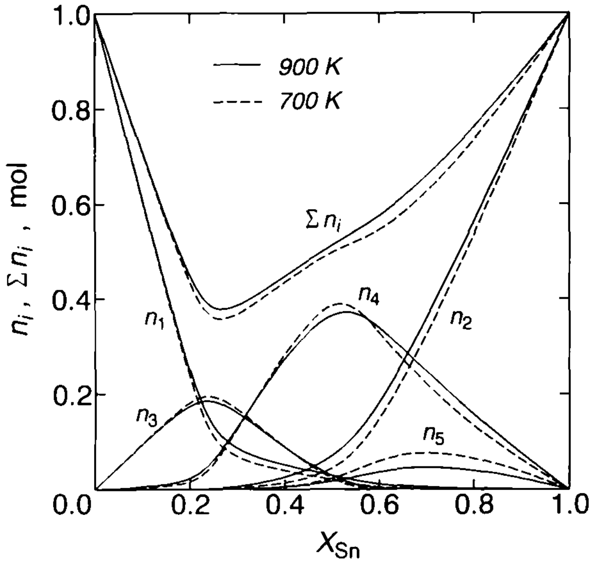

Fig. 6. The calculated mole number of species i (n_i) and the sum of them ($\sum n_i$) when $N_A + N_B$ is 1 mol.

$AuSn_2$ plus A $(= \Delta H_i^0(\partial x_i^*/\partial T)/X_s + A = D_i;\ i = 3, 4, 5)$. Apparently, D_3 and D_4 are in the opposite direction from curve A in Fig. 5. Similar results between D_4 and D_5 are recognized also. Further, it is clearly seen that A does not vary linearly, because this liquid is not a simple binary alloy, but a five-component alloy. The small minimum of A shown in Fig. 5 is another result of the minimum of $C_p^{\prime}$ near 75 at% Au. In conclusion, the existence of AC does not always cause a peak of specific heat capacity when plural AC exists.

It became clear from the above discussion that the specific heat capacity, heat of mixing, and activity in a wide temperature range are all described by this model assuming Au_3Sn, AuSn, and $AuSn_2$. Therefore, these thermodynamic properties do not contradict each other at all. They are only different thermodynamic aspects of the Au–Sn liquid itself.

In Fig. 6 the mole numbers of species i (n_i) and sum of them ($\sum n_i$) which were calculated assuming $(N_A + N_B)/\text{mol} = 1$ are shown. As clearly seen, $\sum n_i$ shows a minimum at the stoichiometric composition of Au_3Sn, which implies that the liquid is the most ordered at 75 at% Au. Therefore there would be a close relation between this minimum and some anomalies observed in this region, and thus, we expect that the results of X-ray measurements would be possibly explained if the plural AC are considered.

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