

**THE HEAT CAPACITY AND ENTHALPY OF SOME HUME–ROTHERY PHASES FORMED BY COPPER, SILVER AND GOLD. PART II.
Cu + Ge, Cu + Sn, Ag + Sn, Au + Sn, Au + Pb SYSTEMS**

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ABSTRACT

The enthalpy and heat capacity of several alloy compositions in the Cu + Ge, Cu + Sn, Ag + Sn, Au + Sn and Au + Pb systems have been determined by differential scanning calorimetry for temperatures between 230 and 1000 K. The following compositions have been studied: $\text{Cu}_{0.87}\text{Ge}_{0.13}$, $\text{Cu}_{0.75}\text{Ge}_{0.25}$, $\text{Cu}_{0.75}\text{Sn}_{0.25}$, $\text{Cu}_{0.85}\text{Sn}_{0.15}$, $\text{Cu}_{0.834}\text{Sn}_{0.166}$, $\text{Ag}_{0.865}\text{Sn}_{0.135}$, $\text{Ag}_{0.75}\text{Sn}_{0.25}$, $\text{Au}_{0.875}\text{Sn}_{0.125}$, $\text{Au}_{0.34}\text{Sn}_{0.66}$, $\text{Au}_{0.2}\text{Sn}_{0.8}$, $\text{Au}_{0.67}\text{Pb}_{0.33}$, $\text{Au}_{0.34}\text{Pb}_{0.66}$.

INTRODUCTION

The work described in this paper is part of a larger programme to investigate the thermal properties of a large number of Hume–Rothery phases formed by copper, silver and gold. In the first part of this programme we described the measurements carried out on the alloys containing antimony and bismuth [1]; here we describe the measurements conducted on some Hume–Rothery phases formed by the Group IB elements with germanium, tin and lead. In addition to the thermal property data this study was intended to provide valuable phase diagram information.

EXPERIMENTAL

The alloys used in this investigation were prepared from high purity materials (99.9995%); the Cu, Ge, Sn and Pb were supplied by Preussag AG,

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and the Ag and Au by Degussa. The two components were melted together in sealed silica capsules and then quenched, ground and annealed for several days 5 K below the solidus temperature. Discs were prepared from the crushed powder of the alloy and were then annealed to remove any stored energy effects caused by the cold work. Further details of the preparation are given elsewhere [2]. The samples were examined and identified by X-ray diffraction and metallographic analysis.

Measurements were made using a Perkin-Elmer model 2 differential scanning calorimeter (DSC). The output signal from the DSC was measured with a digital voltmeter and recorded on paper tape. The treatment of the data to yield enthalpy and heat capacity values has been described elsewhere [1,3,4]. The performance of the apparatus was checked by measuring the heat capacity of silver; the scatter of individual points from the $C_p(T)$ curve due to Hultgren et al. [5] had standard deviations of 1% and 2%, respectively, for the temperature ranges 250–600 K and 600–1000 K.

RESULTS AND DISCUSSION

In this paper, molar thermodynamic properties are for 1 mole of A_xB_{1-x} , where $x < 1$ and A is Cu, Ag or Au, and B is Ge, Sn or Pb.

Cu + Ge system

The phase diagram reported by Hansen and Anderko [6] shows the presence of two phases at room temperature: the ζ -phase which decomposes peritectically at 1096 K, and the ϵ_1 -phase which decomposes at 908 K to a mixture of ϵ - and ϵ_2 -phases.

The ζ -phase was investigated with an alloy composition of $Cu_{0.87}Ge_{0.13}$ which lies close to the copper-rich boundary of the homogeneity range of this phase. The ζ -phase possesses a close-packed hexagonal structure and has an electron/atom ratio of 21/14. The heat capacity and enthalpy of the ζ -phase were determined for temperatures between 229 and 984 K and are given in Fig. 1. The $C_p(T)$ relationship is given by eqn. (1)

$$C_p/(\text{J K}^{-1} \text{ mole}^{-1}) = 23.33 + 6.9 \times 10^{-3}(T/\text{K}) - 75077(T/\text{K})^{-2} \quad (1)$$

As can be seen from Fig. 1, no transformations occur in the ζ -phase in the temperature interval studied; these observations are in line with extant phase diagram data [6].

The ϵ_1 -phase exists in a compositional range corresponding to an electron/atom ratio of 21/12 and possesses a distorted orthorhombic structure; the high-temperature phase, ϵ , has a close-packed hexagonal structure. This phase was studied by making C_p measurements at two different compositions: $Cu_{0.755}Ge_{0.245}$ and $Cu_{0.745}Ge_{0.255}$; the C_p and enthalpy results are given in Fig. 2. The C_p values recorded for these two compositions lie within the range of experimental uncertainty. The $C_p(T)$ relationship for $Cu_{0.745}Ge_{0.255}$ in the temperature interval 298–700 K is given by eqn. (2).

$$C_p/(\text{J K}^{-1} \text{ mole}^{-1}) = 24.03 + 5.65 \times 10^{-3}(T/\text{K}) - 82316(T/\text{K})^{-2} \quad (2)$$

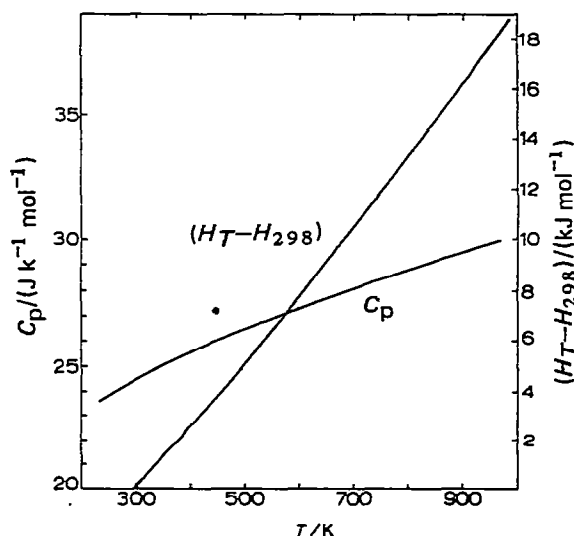


Fig. 1. C_p and $(H_T - H_{298})$ for the ζ -phase alloy $\text{Cu}_{0.87}\text{Ge}_{0.13}$.

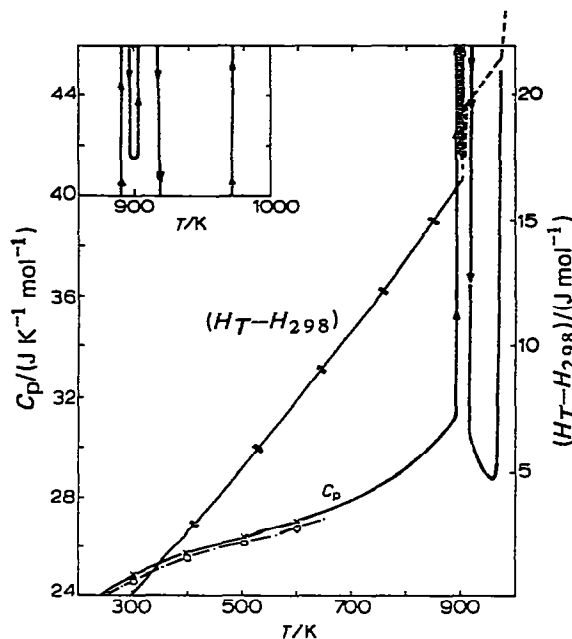


Fig. 2. C_p and $(H_T - H_{298})$ for the ϵ_1 -phase alloy. $x\text{---}x$, $C_p(\text{Cu}_{0.745}\text{Ge}_{0.255})$; $o\text{---}o$, $C_p(\text{Cu}_{0.755}\text{Ge}_{0.245})$; --- , $(H_T - H_{298})$ for $\text{Cu}_{0.745}\text{Ge}_{0.255}$.

As can be seen from Fig. 2 three endotherms were observed in the $C_p(T)$ curve for $\text{Cu}_{0.745}\text{Ge}_{0.255}$; these occurred at 893 K, 913 K and 973 K and corresponded to the following transformations, respectively, (i) the eutectoid formation of the ϵ_2 -phase at 885 K [6], (ii) the peritectic dissociation of the ϵ_1 -phase at 908 K [6], and (iii) the peritectic dissociation of the ϵ_2 -phase at 973 K [6]. Thus, the occurrence of these endotherms substantiates the extant phase diagram [6].

Cu + Sn

The phase diagram for this system indicates that only two phases, η' and ϵ , exist at ambient temperatures, but that the β , γ , δ and ζ -phases exist at higher temperatures. The ϵ -phase, which possesses an orthorhombic structure, has an electron/atom ratio of 21/12 for the composition $\text{Cu}_{0.75}\text{Sn}_{0.25}$ studied in this investigation. The only extant C_p data available for this system are the $C_{p,298}$ values for $\text{Cu}_{0.979}\text{Sn}_{0.021}\text{Cu}_{0.956}\text{Sn}_{0.044}$ and $\text{Cu}_{0.936}\text{Sn}_{0.064}$ due to Honda and Tokunaga [7]. Values of C_p and $(H_T - H_{298})$ were determined for the temperature interval 235–984 K; the results (given in Fig. 3) indicate the presence of two endotherms occurring at 950 K and 985 K*, corresponding to the $\epsilon \rightarrow \gamma$ transformation at 949 K [6] and the peritectic decomposition of the γ -phase at 983 K. Thus, the C_p data are in good agreement with the accepted phase diagram [6]. The $C_p(T)$ relation-

* Estimated value, as peak not obtained at 984 K.

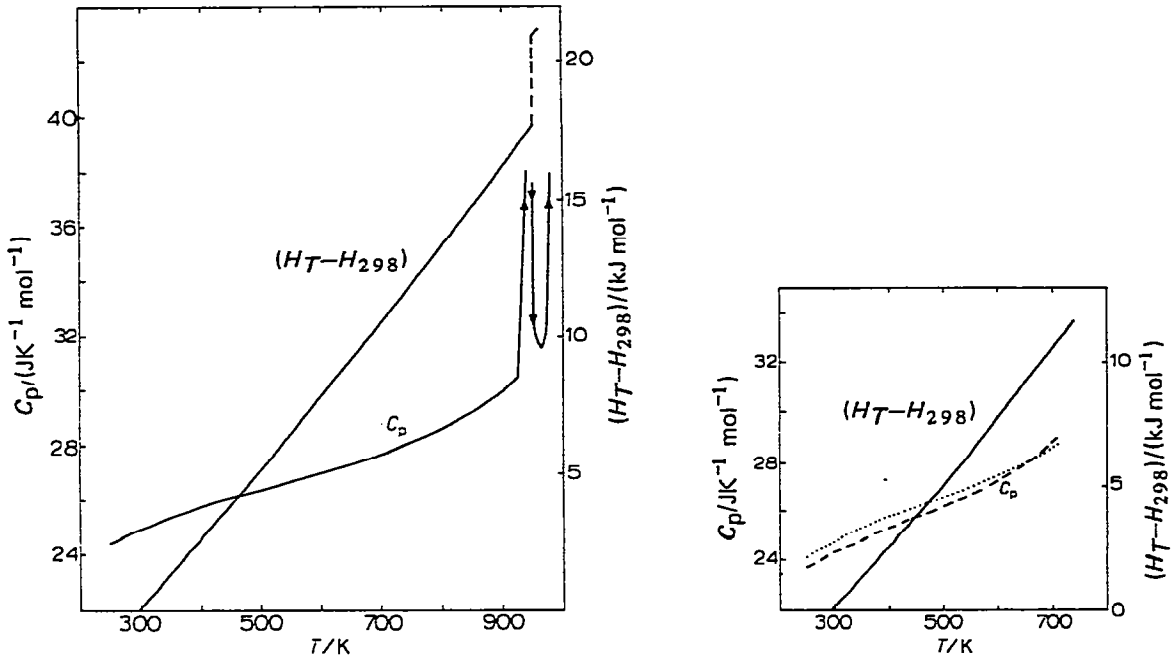


Fig. 3. C_p and $(H_T - H_{298})$ for the ϵ -phase alloy $\text{Cu}_{0.75}\text{Sn}_{0.25}$.

Fig. 4. C_p and enthalpy data for $\text{Cu}_{0.85}\text{Sn}_{0.15}$ and C_p for $\text{Cu}_{0.834}\text{Sn}_{0.166}$. —, $(H_T - H_{298})$; ---, C_p for $\text{Cu}_{0.85}\text{Sn}_{0.15}$; ·····, C_p for $\text{Cu}_{0.834}\text{Sn}_{0.166}$.

ship for $\text{Cu}_{0.75}\text{Sn}_{0.25}$ for temperatures between 250 and 800 K is given by eqn. (3). The approximate values, $\Delta H_{\text{tr}} \approx 3.3 \text{ J mole}^{-1}$

$$C_p/(\text{J K}^{-1} \text{ mole}^{-1}) = 23.04 + 6.89 \times 10^{-3}(T/\text{K}) - 20079(T/\text{K})^{-2} \quad (3)$$

and $\Delta S_{\text{tr}} \approx 3.5 \text{ J K}^{-1} \text{ mole}^{-1}$ were obtained for the $\epsilon \rightarrow \gamma$ transformation from the data presented in Fig. 3.

Heat capacities were determined for two alloys with compositions of $\text{Cu}_{0.834}\text{Sn}_{0.166}$ and $\text{Cu}_{0.85}\text{Sn}_{0.15}$ for temperatures between 235 and 738 K; the results are shown in Fig. 4 and the $C_p(T)$ relationships are given in eqns. (4) and (5), respectively.

$$C_p/(\text{J K}^{-1} \text{ mole}^{-1}) = 22.02 + 9.32 \times 10^{-3}(T/\text{K}) - 13105(T/\text{K})^{-2} \quad (4)$$

$$C_p/(\text{J K}^{-1} \text{ mole}^{-1}) = 20.30 + 11.7 \times 10^{-3}(T/\text{K}) - 36752(T/\text{K})^{-2} \quad (5)$$

Ag + Sn

The reported phase diagram [6] for the Ag + Sn system shows the presence of two Hume-Rothery phases, ζ and ϵ . The ζ -phase has a close-packed hexagonal structure and occurs at an electron/atom ratio of 21/14 for the composition $\text{Ag}_{0.833}\text{Sn}_{0.167}$; however, the ζ -phase possesses a wide range of homogeneity and this extends at higher temperatures to include the composition $\text{Ag}_{0.795}\text{Sn}_{0.205}$, which corresponds to an electron/atom ratio of

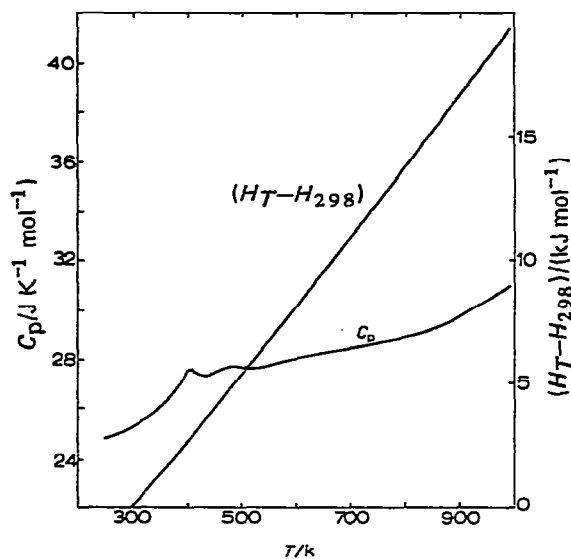


Fig. 5. C_p and $(H_T - H_{298})$ for the ζ -phase alloy $\text{Ag}_{0.865}\text{Sn}_{0.135}$.

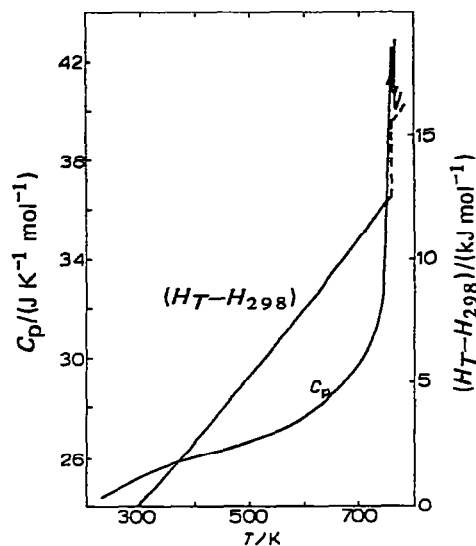


Fig. 6. C_p and $(H_T - H_{298})$ for the ϵ -phase alloy $\text{Ag}_{0.75}\text{Sn}_{0.25}$.

21/13. The alloy composition studied here, $\text{Ag}_{0.865}\text{Sn}_{0.135}$, lies close to the silver-rich boundary of the homogeneity range of the ζ -phase. Heat capacities and enthalpies of this alloy were measured for temperatures between 229 and 984 K; the results are given in Fig. 5. Two small peaks were observed in the $C_p(T)$ curve around 400 K and 480 K. These endotherms which have a combined enthalpy of transition of ca. 100 J mole^{-1} do not appear to be related to any known phase diagram characteristics [6]. In fact, these thermal effects seem very similar to those observed in the γ -phase of $\text{Cu} + \text{Zn}$, $\text{Cu} + \text{Cd}$, $\text{Ag} + \text{Zn}$ and $\text{Ag} + \text{Cd}$ alloys [8] occurring at similar temperatures and producing similar ΔH_{tr} values. In the case of γ -phase alloys it was concluded that the endotherms were probably produced by a short-range ordering phenomenon [8]. However, this phenomenon could also be due to constitutional vacancies as described recently by Nover and Schubert [9].

The ϵ -phase has a distorted, close-packed, hexagonal structure and corresponds to an electron/atom ratio of 21/12. The ϵ -phase alloy studied here had a composition of $\text{Ag}_{0.75}\text{Sn}_{0.25}$. Heat capacities and enthalpies were determined for temperatures between 235 and 780 K; the results are shown in Fig. 6. The $C_p(T)$ relationship for the temperature interval 298–600 K is given by eqn. (6).

$$C_p/(\text{J K}^{-1} \text{ mole}^{-1}) = 23.18 + 7.18 \times 10^{-3}(T/\text{K}) - 8779(T/\text{K})^{-2} \quad (6)$$

The peritectic decomposition of the ϵ -phase has been reported to occur at 753 K [6]; the peak in the $C_p(T)$ curve recorded here occurred at 764 K, and on the basis of the enthalpy data presented in Fig. 6, the ΔH_{tr} had a value ca. 3.1 kJ mole^{-1} .

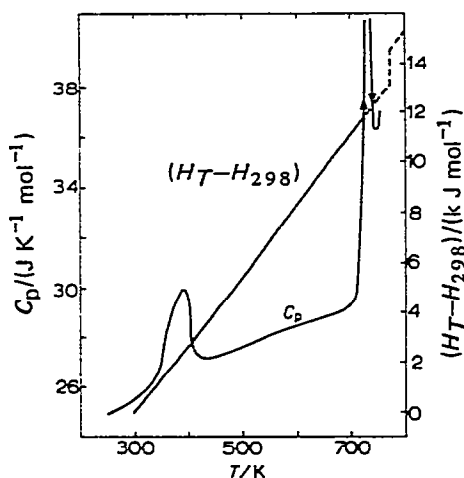


Fig. 7. C_p and $(H_T - H_{298})$ for the ζ -phase alloy $\text{Au}_{0.875}\text{Sn}_{0.125}$.

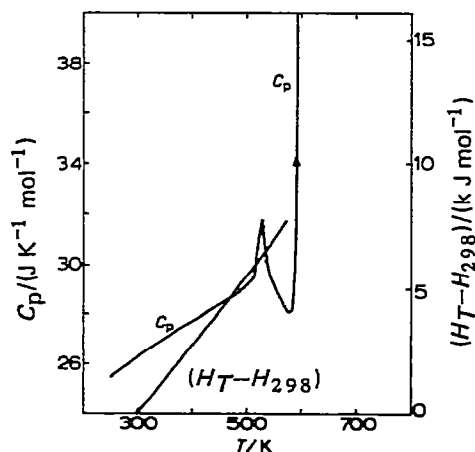


Fig. 8. C_p and $(H_T - H_{298})$ for the alloy $\text{Au}_{0.34}\text{Sn}_{0.66}$.

Au + Sn

The phase diagram for the Au + Sn system due to Hansen and Anderko [6] shows the existence of four phases: the ζ -phase AuSn , AuSn_2 and AuSn_4 ; C_p and $(H_T - H_{298})$ data are presented for all but the last of these phases. In addition, Schubert et al. [10] have reported the existence of two hexagonal phases: Au_{10}Sn and $\text{Au}_{83}\text{Sn}_{17}$. The ζ -phase has a close-packed hexagonal structure and occurs at an electron/atom ratio of 21/14 but the homogeneity range extends to a composition corresponding to an electron/atom ratio of 21/13. The composition of the ζ -phase studied in this investigation was at $\text{Au}_{0.875}\text{Sn}_{0.125}$; the results of this investigation are presented in Fig. 7. A peak in the $C_p(T)$ curve was observed at ca. 390 K; an enthalpy of transition of around 100 J mole^{-1} was associated with this bulge in the $C_p(T)$ curve. The characteristics of this endotherm are similar to those reported for the γ -phase alloys in the systems Cu + Zn, Ag + Zn, Cu + Cd, Ag + Cd, and the ζ -phase alloy for Ag + Sn. It was concluded that the endotherms in the γ -phase were probably produced by a short-range ordering phenomenon. Further peaks in the $C_p(T)$ curve were observed at 730 K and at ca. 750 K and can be assigned to the $\zeta \rightarrow \zeta + \text{liquid}$ and the peritectic decomposition, respectively. The enthalpy of transition associated with these two peaks in the $C_p(T)$ curve had a cumulative value of ca. 1.3 kJ mole^{-1} .

The AuSn_2 phase has an orthorhombic structure. The sample studied in this investigation had the composition $\text{Au}_{0.34}\text{Sn}_{0.66}$; the results are presented in Fig. 8. A peak in the $C_p(T)$ curve was observed at 527 K. Examination of the phase diagram [6] indicates that an endotherm at 525 K would be anticipated if the composition of the sample lies outside the Sn-rich boundary of the homogeneity range of this phase. Further peaks in the $C_p(T)$ curve at 603 and 630 K * correspond to the transitions: $\text{AuSn}_2 + \text{liquid} \rightarrow \text{AuSn} +$

* Estimated transition temperature as only the beginning of the C_p peak was monitored.

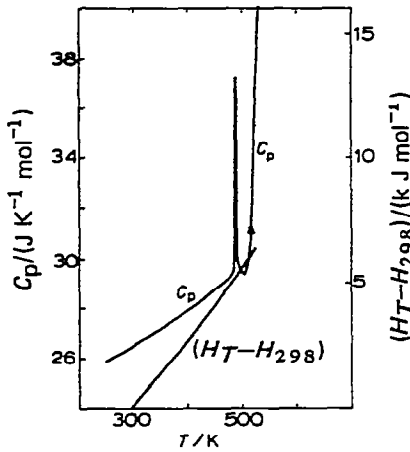


Fig. 9. C_p and $(H_T - H_{298})$ for the alloy $Au_{0.2}Sn_{0.8}$.

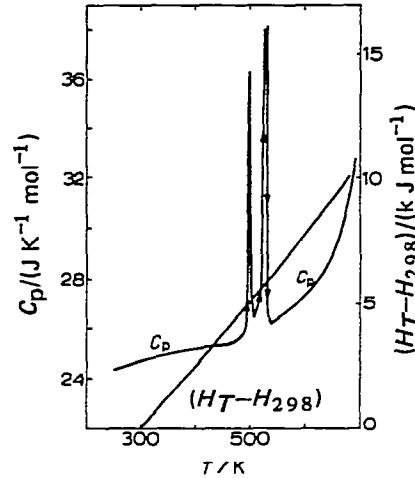


Fig. 10. C_p and $(H_T - H_{298})$ for the alloy $Au_{0.67}Pb_{0.33}$.

liquid and $AuSn + \text{liquid} \rightarrow \text{liquid}$, respectively, and are in reasonable agreement with the transition temperatures of 582 K and 615 K reported by Hansen and Anderko [6].

The $AuSn_4$ phase also possesses an orthorhombic structure according to Hansen and Anderko [6]. Heat capacities and enthalpies were determined between 238 and 535 K for a sample of composition $Au_{0.2}Sn_{0.8}$. The results are presented in Fig. 9. The results show two peaks in the $C_p(T)$ curve occurring at 488 K and 529 K*, respectively. These are in good agreement with transition temperatures listed by Hansen and Anderko [6] of 490 K for the transition $AuSn_4 + \text{liquid} \rightarrow AuSn_2 + \text{liquid}$, and 525 K for the transition $AuSn_4 + \text{liquid} \rightarrow AuSn_2 + \text{liquid}$, respectively. The $C_p(T)$ relationship is given by eqn. (7) for temperatures between 298 and 480 K.

$$C_p/(\text{J K}^{-1} \text{ mole}^{-1}) = 21.0 + 16.6 \times 10^{-3}(T/\text{K}) + 47324(T/\text{K})^{-2} \quad (7)$$

Au + Pb

The phase diagram reported by Hansen and Anderko [6] cites the existence of two compounds in this system, viz. Au_2Pb and $AuPb_2$. It has been reported [11,12] that the Au_2Pb phase is unstable below some undetermined temperature. The reported structures for $AuPb_2$ and Au_2Pb are body-centred tetragonal and a structure isotypic with $MgCu_2$, respectively.

The heat capacity and enthalpy for $Au_{0.67}Pb_{0.33}$ were determined for temperatures between 239 and 689 K; the results are presented in Fig. 10. The $C_p(T)$ relationship for temperatures between 250 and 450 K is given by eqn. (8).

$$C_p/(\text{J K}^{-1} \text{ mole}^{-1}) = 24.43 + 2.56 \times 10^{-3}(T/\text{K}) - 42324(T/\text{K})^{-2} \quad (8)$$

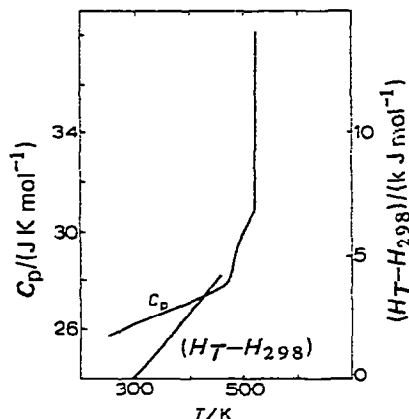


Fig. 11. C_p and $(H_T - H_{298})$ for the alloy $\text{Au}_{0.34}\text{Pb}_{0.66}$.

Two endotherms were recorded at 496 and 525 K. These findings are in agreement with the phase diagram due to Hansen and Anderko [6] which shows that thermal effects for $\text{Au}_{0.33}\text{Pb}_{0.67}$ occur at the eutectic (488 K) and peritectic temperatures (527 K). The sharp increase in C_p between 650 and 689 K indicates that a further transition probably occurs at ca. 700 K and corresponds to the peritectic decomposition at 691 K for $\text{Au}_{0.67}\text{Pb}_{0.33}$.

The heat capacity and enthalpy for the alloy $\text{Au}_{0.34}\text{Pb}_{0.66}$ were determined between 235 and 552 K; the results are presented in Fig. 11. The endotherm recorded at 525 K corresponds to the peritectic decomposition of this phase. The bulge in the $C_p(T)$ curve between 475 and 520 K may be due to a thermal effect associated with the eutectic temperature. The $C_p(T)$ relationship for temperatures between 250 and 470 K is given by eqn. (9).

$$C_p/(\text{J K}^{-1} \text{ mole}^{-1}) = 24.34 + 7.39 \times 10^{-3}(T/\text{K}) - 29921(T/\text{K})^{-2} \quad (9)$$

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