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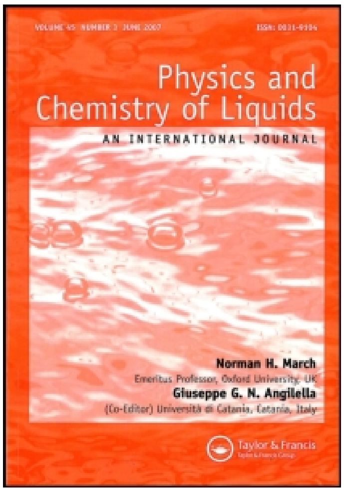

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THERMODYNAMIC INVESTIGATION OF SOLID AND LIQUID Au–Te ALLOYS

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The heat content of solid and liquid $AuTe_2$ compound was measured from 298 K to T (471–1022 K) on heating (drop method) with the help of a Tian-Calvet calorimeter. The heat capacity of the liquid compound as well as its enthalpy of fusion were deduced. The enthalpy of the liquid decreases strongly when temperature increases especially for $T > 923$ K. Such a behaviour cannot be explained easily by the existence of a short-range order since the enthalpy of formation is only weakly negative.

The enthalpies of dissolution of Au and $AuTe_2$ in Au–Te melts were also determined by direct reaction calorimetry at 728 K with respect to concentration ($0 < x_{Au} < 0.18$ and $0 < x_{AuTe_2} < 0.27$). With the help of the heat content data determined previously we calculated the enthalpy of formation of the $AuTe_2$ compound at 298 K (-3.3 kJ per mole of atoms). Such a low negative value as well as the low melting temperature agree well with the assumption of some associated state of the liquid in spite of the weakly negative enthalpy of mixing.

KEY WORDS: Calorimetry, Enthalpy, Enthalpy of mixing, Heat capacity, $AuTe_2$.

1 INTRODUCTION

For more than thirty years our experimental and theoretical work has been devoted to the investigation of liquid metallic alloys showing negative departures from thermodynamic ideality. In the case of very strong departures (minimum of the enthalpy of mixing less than $-40\,\mathrm{kJ \cdot mol^{-1}}$) such a behaviour has been explained by the existence in the liquid of associations (or hetero-clusters) corresponding in many cases to the stoichiometry of congruently high-melting compounds[1]. Such strongly associated metallic systems exhibit only very weak temperature dependence in the temperature range where measurements can be performed since the associated species are thermodynamically very stable.

On the contrary, there is a special class of alloys, exhibiting only one intermediate compound with low melting point, which show a peculiar behaviour corresponding to a moderately associated state. These melts can show in a temperature range where measurements are possible what we called a "short-range order-disorder transition"[2] due to the destruction of their short-range order when temperature increases. The Ge–Te, Au–Pb, Au–Te and Au–Sb melts belong to this class of liquid alloys. In the case of Ge–Te melts we pointed out[3] the occurrence of such a transition at the Te-rich eutectic composition. Our calorimetric investigation on the Au–Pb liquids[4] in the whole range of concentration confirmed the surprising very large temperature dependence of their enthalpy of mixing for $695 < T/K < 1123$ suspected by Okamoto and Massalski[5]. Finally we suspected a similar behaviour in the case of the Au–Te melts measuring their enthalpy of mixing with respect to temperature[6]. Since the thermodynamic properties of this last system seem to be strongly connected with the existence of the $AuTe_2$ compound the aim of this work was to determine the thermodynamic properties of this phase, especially in the liquid state.

2 CALORIMETRIC METHODS

The apparatus employed was a very high-temperature ($T/K < 1800$) Tian-Calvet calorimeter. The drop methods used (direct reaction calorimetry and enthalpimetry) were already described[7].

The molar heat content variation of $AuTe_2$ from 298 K to T ($471 \leqslant T/K \leqslant 1022$) was deduced from the heat effects corresponding to drops of solid $AuTe_2$ samples (#30 mg) into an empty graphite crucible placed in the laboratory cell of the calorimeter. The measurements were repeated about ten times at each temperature. The samples were synthetized by dissolving pure solid gold in pure liquid tellurium in suitable proportions and heating the mixture at 750 K up to homogenization. After annealing at a temperature just below the melting point (725 K), we verified their structural state by X-ray diffraction. As shown on Figure 1 (upper part) the diffractogram obtained agrees well with the ASTM files. These samples were used for the heat content determinations. However when annealed at 693 K the samples gave the diffractogram shown on the bottom of Figure 1. These differences lead to the evidence for a transition in the solid state. Such a conclusion agrees well with the unknown thermal arrest at 722 K we pointed out in a previous work[6] from differential thermal analysis.

The partial enthalpies of dissolution of Au and of $AuTe_2$ in the melt, $h^{\text{diss}}(\text{Au})$ and $h^{\text{diss}}(\text{AuTe}_2)$, were deduced from the heat effects corresponding to successive additions of small quantities of Au or $AuTe_2$ (about 20 to 50 mg according to the concentration range) at T_0 (near 298 K) into the same bath placed in a graphite crucible at the bottom of the calorimetric cell at temperature T. Before the first addition of Au or $AuTe_2$ the melt was pure tellurium (about 1 g).

Then the thermal effects in the case of adding Au to the Au–Te melt correspond to the reaction:

$$n\text{Au}(\text{cr}, \text{T}_0) + m\text{Au}_x\text{Te}_y(1, \text{T}) \longrightarrow (n+m)\text{Au}_{x+dx}\text{Te}_{y-dy}(1, \text{T})$$

Each heat effect corresponding to successive additions of Au (or $AuTe_2$) leads to the partial enthalpy of solute in the binary alloy against composition with respect to pure solid sample at T_0. Taking into account the enthalpy of fusion of gold (neglecting any temperature dependence) and its enthalpy change from T_0 to T deduced from[8] or the heat content of $AuTe_2$ derived from our previous measurements by enthalpimetry, we deduced the enthalpy of mixing of the Au–Te melt with reference to both pure liquid components.

The pure metals used were purchased from Koch–Light with metallic impurities less than 10^{-3} mass%. The calibration of the calorimeter was performed by adding some

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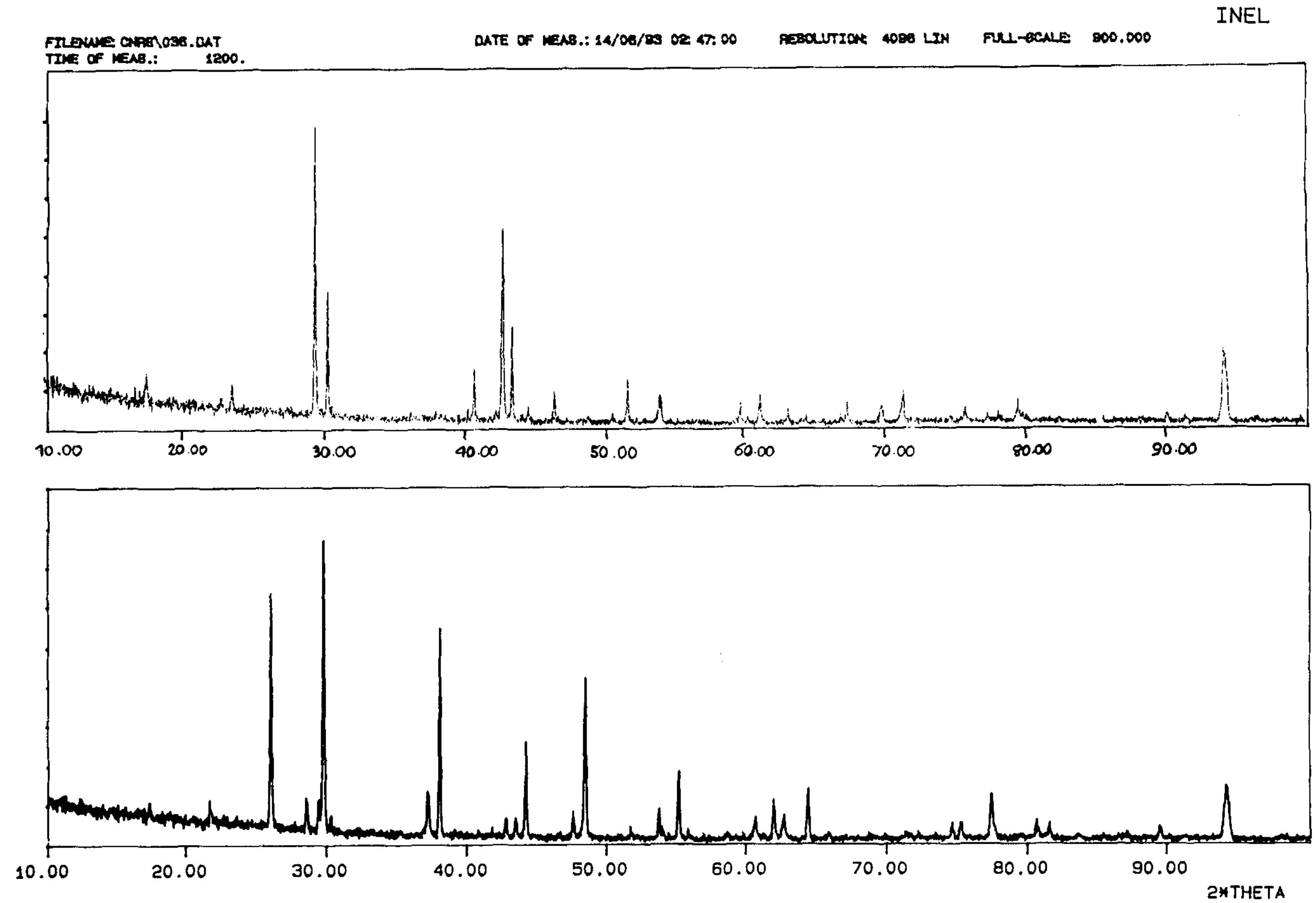

Figure 1 X-ray diffractograms of $AuTe_2$. Upper part: After annealing at 378 K. Lower part: Quenched at room temperature after annealing at 693 K.

Table 1 Heat content of $AuTe_2$ from 298 to T/K referred to a mole of compound.

T(K)	*H(T) – H(298 K)* kJ·mol^{-1}	*T(K)*	*H(T) – H(298 K)* kJ·mol^{-1}
471	4.44	823	34.29
570	7.35	853	35.09
652	9.42	880	35.92
704	10.83	885	36.00
713	11.22	892	36.31
738	30.98	923	37.92
743	31.09	932	38.06
751	31.48	953	37.81
763	31.74	981	38.16
777	32.38	998	38.67
793	32.92	1022	38.92
805	33.44		

small pieces of α-alumina (U.S. National Bureau of Standards) the enthalpy change of which from T_0 to T is well-known[9].

3 RESULTS

3.1 Enthalpimetry

The values of the enthalpy of $AuTe_2$ from 471 to 1022 K are given in Table 1 and shown on Figure 2. At each temperature the value listed is the average of about ten determinations. In the solid state ($T^{fus} < 737$ K) our data agree well with the values calculated from the C_p-data of Andon *et al.*[10] and of Itagaki[11]. Since it was not the purpose of this work to determine the thermodynamic properties of $AuTe_2$ in the solid state we measured its enthalpy only at four temperatures. Then we did not derived its heat capacity.

The jump at 737 K lead to a value of the enthalpy of fusion (19.1 kJ·per mol of atoms) somewhat higher than that we obtained previously[6] (17.3 kJ·mol^{-1}) from a more indirect method. It is near that determined by Andon *et al.*[10] (18.6 kJ·mol^{-1}) but very different from that of Itagaki[11] (15.86 kJ·mol^{-1}) and T. Ishida *et al.*[12] (15.3 kJ·mol^{-1}). These two last data are very close to the enthalpy of fusion calculated from additivity (15.84 kJ·mol^{-1}).

The results obtained in the liquid state exhibit a strong temperature dependence as shown on Figure 2. They can be fitted according two procedures. In the first one the data corresponding to the whole temperature range investigated can be fitted according to the following equation:

$$H(\mathrm{T/K}) - H(298\,\mathrm{K})/\mathrm{kJ\cdot mol^{-1}} = -35.33 + 0.133\,\mathrm{T} - 59.10^{-6}\,\mathrm{T}^2$$

which leads to:

$$C_p/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = 133 - 0.118\,10^{-3}\mathrm{T}$$

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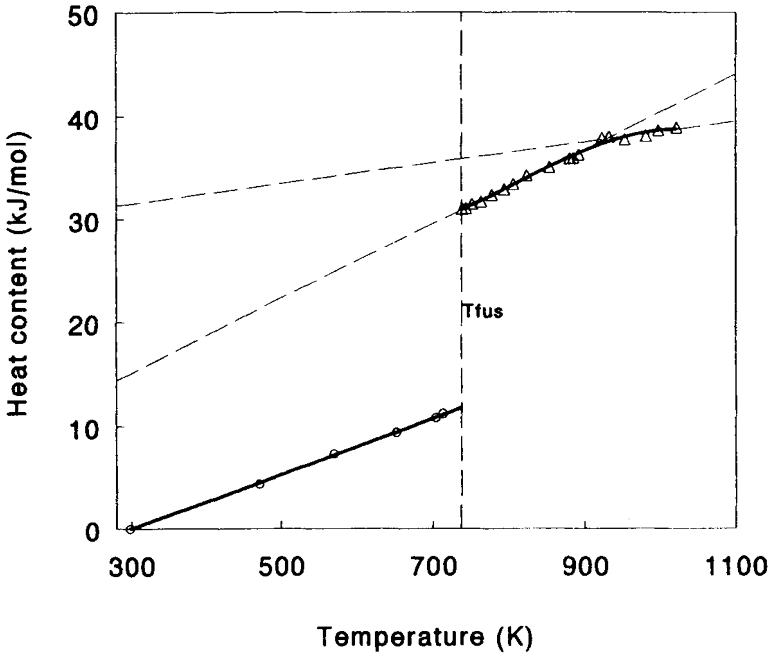

Figure 2 Heat content of $AuTe_2$ from 298 to T/K referred to a mole of atoms. Solid points: This work. The solid line below the melting point corresponds to the results of [10] and [11]. The full and the dotted lines in the liquid state correspond to two different fitting of our data (see text).

In the second case we considered two different temperature ranges below and above 923 K (dotted lines of Figure 2). They correspond to a low temperature part ($C_P = 35.9\,J{\cdot}K^{-1}{\cdot}mol^{-1}$) and to a high temperature one ($C_P = 10.1\,J{\cdot}K^{-1}{\cdot}mol^{-1}$). Such a behaviour was already observed in the liquid state by Komarek *et al.*, on the Cd–Sb[13,14] and on the Cu–Sb alloys[15]. Itagaki *et al.*[11] who carried out C_P-measurements only on the low temperature part ($T/K < 873$) obtained a value very close to ours ($38.78\,J{\cdot}K^{-1}{\cdot}mol^{-1}$).

3.2 *Enthalpies of dissolution*

The results of the measurements of the enthalpy of dissolution at 728 K of Au(cr, 298 K) and $AuTe_2$(cr, 298 K) in Au–Te melts are listed in Table 2 with reference to mole fractions of Au and $AuTe_2$ respectively. The partial enthalpy of gold referred to Au(cr, 298 K) in liquid melts at 728 K (Fig. 3) is in good agreement with the values deduced from our previous measurements by direct reaction calorimetry[6] at 737 K. It leads at infinite dilution to the value of $26.49\,kJ{\cdot}mol^{-1}$. The partial enthalpy of $AuTe_2$(cr, 298 K) at 728 K referred to a mole of $AuTe_2$ is shown on Figure 4. The results, more scattered than those of pure Au, lead to 96.24 kJ per mole of $AuTe_2$ at infinite dilution. The two negative values at $x_{Au} = 0.259$ and 0.273 correspond to the $AuTe_2$–Te two phase domain. The liquid–liquid + $AuTe_2$ boundary ($x_{Au} = 0.244$) agrees well with selected data of Okamoto *et al.*[17].

Table 2 Molar enthalpy of dissolution of Au and $AuTe_2$ in Au–Te liquid alloys at 728 K referred to Au(cr, 298 K) and to $AuTe_2$(cr, 298 K) with respect to the mole fraction of Au and $AuTe_2$ respectively.

X_{AuTe_2}	$h^{diss}(AuTe_2)$ (kJ/mol)	X_{Au}	$h^{diss}(Au)$ (kJ/mol)
0.006	96.39	0.013	23.48
0.016	94.69	0.037	20.61
0.026	93.47	0.061	19.20
0.035	91.55	0.083	18.60
0.044	89.93	0.104	18.76
0.054	89.91	0.124	18.30
0.062	94.15	0.144	17.96
0.070	91.42	0.162	17.91
0.078	87.28	0.180	18.11
0.087	89.62	0.197	18.33
0.095	88.61	0.214	17.71
0.103	86.02	0.229	17.79
0.110	80.22	0.244	20.49
0.118	88.16	0.259	– 63.69
0.125	87.27	0.273	– 146.43
0.133	86.05		
0.141	88.63		
0.148	88.80		
0.156	89.94		
0.163	85.37		
0.172	88.13		
0.181	90.53		

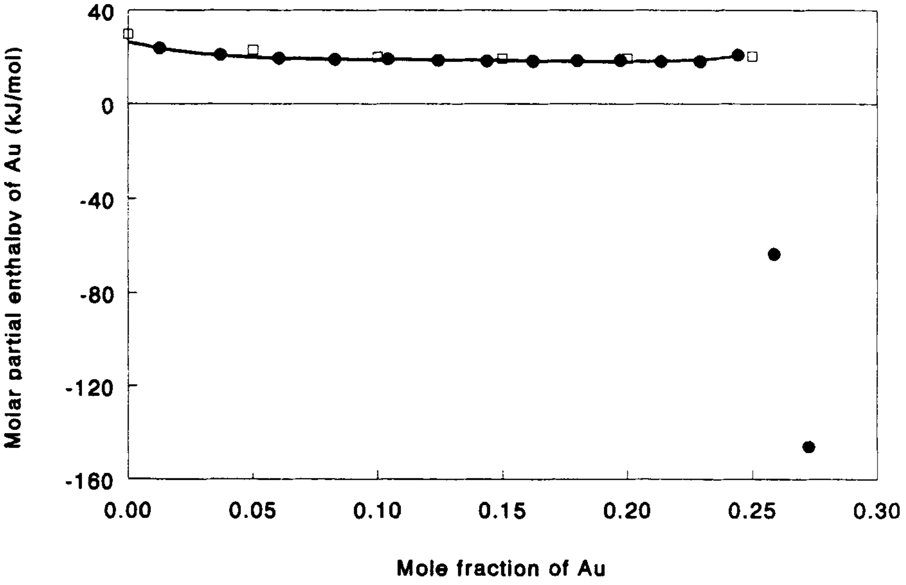

Figure 3 Molar enthalpy of dissolution of Au into Au–Te melts at 728 K referred to a mole of Au (cr, 298 K) and to the mole fraction of Au. Solid circles: This work. Open squares: From reference [10].

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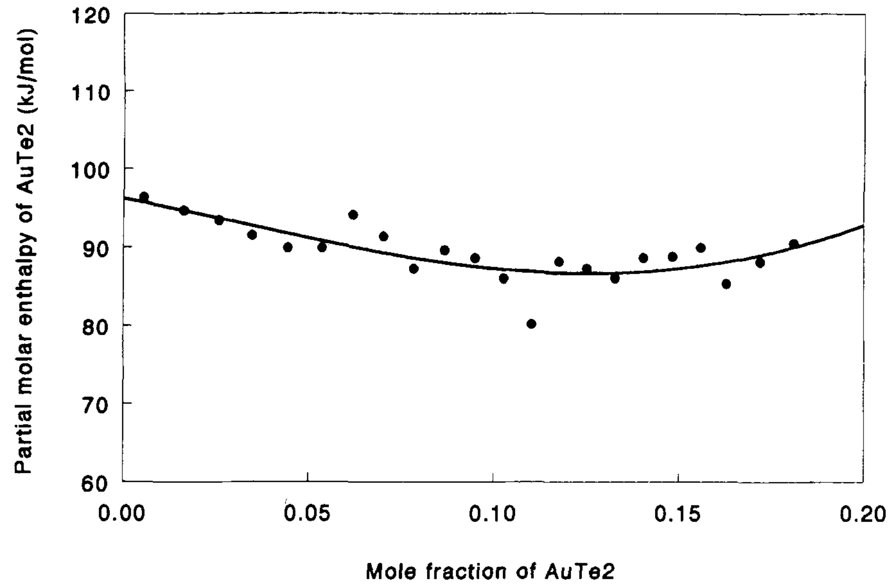

Figure 4 Molar enthalpy of dissolution of $AuTe_2$ into Au-Te melts at 728 K referred to a mole of $AuTe_2$ (cr, 298 K) and to the mole fraction of $AuTe_2$ (This work).

3.3 *Discussion*

From the limiting values ($x_{Au} = 0$) of the enthalpies corresponding to the four following equations:

$$\mathrm{Au(cr, 298\,K) + Te(l, 728\,K) \longrightarrow Au(l, diss.\ in\ Te, 728\,K)} \qquad h_1$$

$$\mathrm{Te(cr, 298\,K) + Te(l, 728\,K) \longrightarrow Te(l, diss.\ in\ Te, 728\,K)} \qquad h_2$$

$$\mathrm{AuTe_2(cr, 298\,K) + Te(l, 728\,K) \longrightarrow Au(l, diss.\ in\ Te, 728\,K)} \qquad h_3$$

we can deduced the enthalpy of formation of $AuTe_2$(cr, 298 K) with reference to the pure solid components at 298 K:

$$\mathrm{Au(cr, 298\,K) + 2\,Te(cr, 298\,K) \longrightarrow AuTe_2(l, cr, 298\,K)} \qquad h_f$$

$$h^f = h_1^\infty + 2h_2 - h_3^\infty$$

h_2 is the heat content of pure tellurium deduced from Hultgren *et al.*[8] (30.42 kJ·mol^{-1}).

We obtain in such a way:

$$h^f(\mathrm{Au_{0.333}Te_{0.667}, cr, 298\,K}) = -3.0\,\mathrm{kJ \cdot mol^{-1}}$$

somewhat more exothermic than our previous determination from direct reaction calorimetry at 737 K(-2.5 kJ·mol^{-1}). The difference can be attributed to an

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excess-C_p different from zero or to the suspected solid state transition between 298 and 737 K.

From vapour pressure measurements Andon *et al.* [10] and Veale and Barrett [16] obtained respectively −4.74 and −3.91 kJ per mole of atoms from the first law in agreement with our data and −6.35 and −6.07 kJ per mole of atoms using the second law.

4 CONCLUSION

Whatever the temperature dependence (drastic change at 923 K or not) our heat content measurements show clearly that the excess-C_p of $AuTe_2$ decreases when temperature increases from the melting point to 1022 K. The exact value of C_p^{xs} cannot be calculated since the heat capacity of supercooled pure gold cannot be evaluated with precision so far its melting temperature. The thermodynamic properties of the $AuTe_2$ melt show clearly the behaviour of an associated liquid since the negative enthalpy of mixing decreases strongly when temperature increases. However the enthalpy of mixing is only weakly negative ($h^f_{\min} = -1.1\ \mathrm{kJ \cdot mol^{-1}}$ for $x_{Au} = 0.4$ at 737 K) and does not correspond to strongly associated systems. The Au–Te melts, as Au–Pb, Au–Sb and Ge–Te, belong to the class of systems the behaviour of which has to be explained from other ways, perhaps assuming homoclustering.

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