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# Thermodynamic investigation of the Ag–Te and Cu–Te eutectic alloys

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## Abstract

The heat contents of solid and liquid rich-Te Ag–Te and Cu–Te eutectics from 298 K to $T$ ($421<T<820$ K and $512<T<800$ K respectively) were measured on heating (drop method) with the help of a high temperature Tian–Calvet calorimeter. The heat capacity of both liquid and solid eutectics as well as their enthalpies of fusion were deduced.

The thermodynamic behaviour of the two eutectics in the liquid state appear very simple. Their strong short-range orders can be explained by one kind of associate the stoichiometry of which corresponds to the single congruently melting compound of the systems, i.e. $Ag_2Te$ and $Cu_2Te$ respectively. Then, the two eutectics investigated can be considered as reference systems for our further works on weakly associated alloys.

*Keywords:* Calorimetry; Enthalpy; Heat capacity; Ag–Te; Cu–Te; Eutectic

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## 1. Introduction

The two binary systems investigated belong to strongly associated alloys in the liquid state as shown by their negative enthalpy of mixing [1,2]. They show only one congruently high melting compound ($Ag_2Te$ and $Cu_2Te$) the stoichiometries of which correspond to the normal valencies of the components. Moreover, the minima of the enthalpy of formation located at these stoichiometries suggest the existence of associations in the liquid state corresponding to these compounds. On the contrary, there is another class of alloys (for example Ge–Te, Au–Pb, Au–Te, Au–Sb), exhibiting also one intermediate compound but with low melting point, which show a peculiar behaviour corresponding to a moderately associated state. These melts often exhibit in a narrow temperature range what we called a short-range order–disorder transition [3] due to the destruction of their short-range order when temperature increases. In the case of the Ge–Te melts we pointed out [4] the occurrence of such a transition at the Te-rich eutectic composition in agreement with the work of DeNeufville [5]. Moreover, in many cases, the short-range order of these liquids cannot be completely explained by the existence of associations corresponding to the congruently melting compound. In particular, their low melting eutectics often show a complex behaviour as for the Ge–Te system. Then the aim of our work is to investigate the complex thermodynamic behaviour of this class of weakly associated liquid eutectics. In a first step we report here the results obtained on strongly associated eutectics. In a next step we will investigate eutectics with complex short-range order, such as Au–Te and Au–Sb.

## 2. Apparatus and method

The coordinates of the Ag–Te and Cu–Te eutectics investigated are respectively $x_{Te}=0.667$, $T=626$ K and $x_{Te}=0.71$, $T=613$ K according to Moffatt [6]. Both solid alloys were synthesized by melting together the pure components in suitable proportions. The pure metals used were purchased from Koch-Light with metallic impurities less than $10^{-3}$ mass%. After some cycles of fusion–crystallization under pure argon atmosphere, they were annealed for two days about 10 K below their melting point and then slowly cooled down at room temperature. We verified from the X-ray diffraction patterns that they correspond to the stable phases according to Moffatt, i.e. $Ag_5Te_3$ + pure Te and CuTe + pure Te respectively. As shown on Fig. 1, the diffractograms obtained agree well with the ASTM files.

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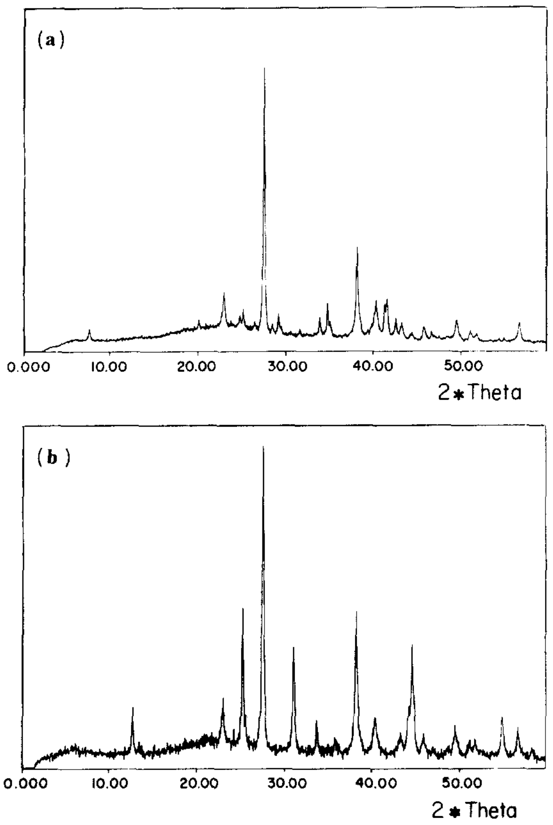

Fig. 1. X-ray diffractograms of the Te-rich (a) Ag–Te and (b) Cu–Te eutectics.

The apparatus employed for the measurements was a high-temperature ($T<1300$ K) Tian–Calvet calorimeter. The drop methods used were already described [7]. The molar heat content variation of the samples from 298 K to $T$ was deduced from the heat effects corresponding to drops of solid samples (about 50 mg) near 298 K into an empty graphite crucible placed in the laboratory cell of the calorimeter at temperature $T$ under argon atmosphere. The measurements were repeated about ten times at each temperature. The calibration of the calorimeter was performed by adding some small pieces of $\alpha$-alumina (US National Bureau of Standards) the enthalpy change of which from $T_0$ to $T$ is well-known [8].

## 3. Results

### 3.1. The Ag–Te eutectic

The values of the enthalpy of the Ag–Te eutectic from 421 to 820 K are given in Table 1 and shown in Fig. 2. In the solid state ($T \leqslant 626$ K) our experimental data can be well fitted according to a linear dependence with temperature:

$$\Delta H(\mathrm{s}) = (-0.939 + 0.0307\ T)\ \mathrm{kJ\ mol^{-1}}$$

then

Table 1
Heat content of the Te-rich Ag–Te eutectic with respect to temperature

| $T$ (K) | $H(T)-H(298\ \mathrm{K})$ ($\mathrm{J\ mol^{-1}}$) | $T$ (K) | $H(T)-H(298\ \mathrm{K})$ ($\mathrm{J\ mol^{-1}}$) |
|---|---|---|---|
| 421 | 3.67 | 627 | 18.98 |
| 460 | 4.73 | 631 | 19.16 |
| 496 | 5.86 | 641 | 19.80 |
| 536 | 7.08 | 647 | 20.04 |
| 565 | 8.05 | 664 | 20.91 |
| 583 | 8.68 | 692 | 21.82 |
| 598 | 8.96 | 726 | 23.38 |
| 615 | 9.64 | 775 | 25.80 |
| 625 | 9.77 | 820 | 27.34 |

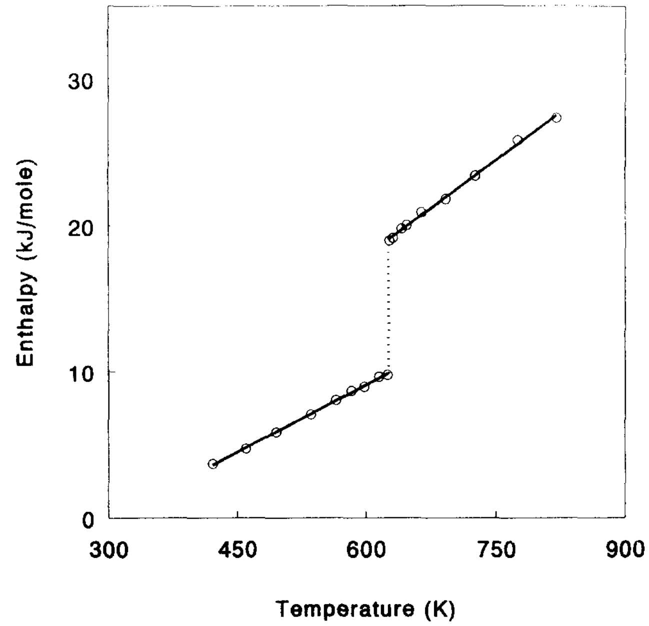

Fig. 2. Heat content of the Te-rich Ag–Te eutectic (each point corresponds to the mean value of about ten determinations).

$$C_P(\mathrm{s}) \sim 30.7\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

The jump between 625 and 627 K leads to the following values of the enthalpy and entropy of fusion respectively:

$$\Delta H^{\mathrm{m}} = \Delta H(\mathrm{l},\ 626\ \mathrm{K}) - \Delta H(\mathrm{s},\ 626\ \mathrm{K})$$
$$= (9.18 \pm 0.11)\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta S^{\mathrm{m}} = (14.66 \pm 0.16)\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

The temperature of fusion deduced from our data agrees well with that of the literature (626 K).

The results obtained in the liquid state can be also well fitted according to a linear dependence since the observed small temperature dependence of $C_P(\mathrm{l})$ is within the experimental uncertainties:

$$\Delta H(\mathrm{l}) = (3.686 + 0.0436\ T)\ \mathrm{kJ\ mol^{-1}}$$

and

$C_P(\mathrm{l}) \sim 43.6$ J K$^{-1}$ mol$^{-1}$

According to the literature, the intermediate compound $Ag_5Te_3$ undergoes a transition at 568 K. The corresponding jump of the enthalpy is too small (76 J mol$^{-1}$) to be observed.

### 3.2. *The Cu–Te eutectic*

The results obtained for the Cu–Te eutectic (Table 2 and Fig. 3) are very similar to those of the previous system.

In the solid state (low temperature region):

$\Delta H(\mathrm{s}) = (-9.689 + 0.0299\ T)$ kJ mol$^{-1}$

and

$C_P(\mathrm{s}) \sim 29.9$ J K$^{-1}$ mol$^{-1}$

In the solid state (high temperature region):

Table 2
Heat content of the Te-rich Cu–Te eutectic with respect to temperature

| $T$ (K) | $H(T)-H(298\ \mathrm{K})$ (J mol$^{-1}$) | $T$ (K) | $H(T)-H(298\ \mathrm{K})$ (J mol$^{-1}$) |
|---|---|---|---|
| 512 | 5.65 | 625 | 20.37 |
| 571 | 7.28 | 629 | 20.57 |
| 598 | 8.15 | 637 | 20.87 |
| 600 | 8.35 | 663 | 21.89 |
| 613 | 10.11 | 675 | 22.42 |
| 615 | 10.25 | 724 | 24.70 |
| 617 | 10.35 | 766 | 26.65 |
| 621 | 10.70 | 800 | 27.92 |
| 623 | 10.91 | | |

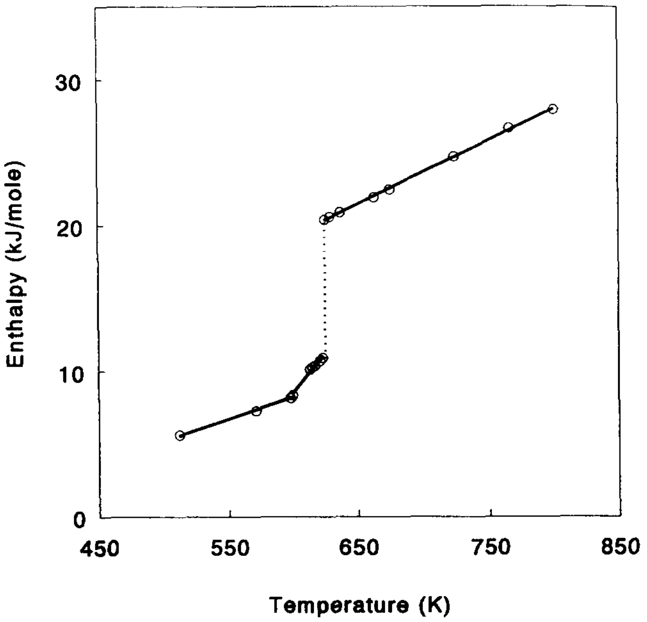

Fig. 3. Heat content of the Te-rich Cu–Te eutectic (each point corresponds to the mean value of about ten determinations).

$\Delta H(\mathrm{s}) = (-57.909 + 0.111\ T)$ kJ mol$^{-1}$

but the corresponding $C_P$ data are unphysical as mentioned later.

In the liquid state:

$\Delta H(\mathrm{l}) = (-7.062 + 0.0438\ T)$ kJ mol$^{-1}$

and

$C_P(\mathrm{l}) \sim 43.8$ J K$^{-1}$ mol$^{-1}$

The small temperature dependence of $C_P(\mathrm{l})$ is within the uncertainties of the measurements, as for the Ag–Te liquid alloys.

The jump between 623 and 625 K leads to the following values of the enthalpy and entropy of fusion respectively:

$$\Delta H^{\mathrm{m}} = \Delta H(\mathrm{l},\ 613\ \mathrm{K}) - \Delta H(\mathrm{s},\ 613\ \mathrm{K}) = (9.09 \pm 0.14)\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta S^{\mathrm{m}} = (14.55 \pm 0.18)\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

The temperature of fusion of the eutectic deduced from the jump of $\Delta H$ is somewhat higher than that of the literature (624 K instead of 613 K).

The data in the solid state show a break at 598 K corresponding to a sharp increase of the enthalpy. Such a behaviour can be easily explained from the phase diagram (Fig. 4). Below 613 K, the alloy is in a two-phase state (pure solid Te + CuTe solid compound). Up to about 600 K the CuTe intermediate compound does not deviate too much from its stoichiometry. On the contrary, between 600 K and 640 K (peritectic temperature) its Cu-content increases strongly when the temperature increases. Its composition varies from $x_{Te} = 0.5$ (600 K) to about 0.48 (640 K). Then, when the temperature increases from 600 K to 623 K, some quantity of free Te reacts with the CuTe solid compound to modify its composition. The sharp increase of enthalpy

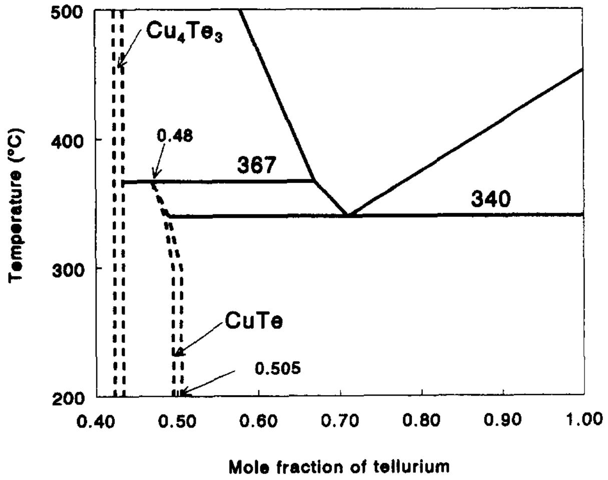

Fig. 4. Phase diagram of the Cu–Te binary system according to Ref. [6].

in this temperature domain corresponds to this reaction and the unusual high value of $C_P$ has no physical meaning.

## 4. Conclusion

In this work, we were mainly interested in the behaviour of the eutectic alloys in the liquid state. One of the thermodynamic functions, the most sensible to eventual short-range order, is the excess heat capacity (departure from the Neumann–Kopp rule). It cannot be calculated here with accuracy since the heat capacities of pure liquid Ag and Cu cannot be extrapolated so far from their melting points. However, from the $C_P$ data of Ref. [9] for Ag and Cu, assuming the same heat capacity values for liquid and undercooled liquid metals, and from the $C_P$ data of Tsuchiya [10] for undercooled Te, the calculations lead to $C_P^{xs}$ values for both eutectic liquid alloys of 4 to 8 J $K^{-1}$ $mol^{-1}$ at 800 K.

Another thermodynamic function sensible to residual short-range order upon melting is the difference between the experimental enthalpy of melting $\Delta H^m$ and the value calculated according to additivity $\Sigma x_i \, \Delta H_i^m$:

$$\delta\Delta H = \Delta H^m - \Sigma x_i \, \Delta H_i^m$$

We found in such a way −6.46 and −7.11 kJ $mol^{-1}$ for the Ag–Te and Cu–Te eutectics respectively, taking the enthalpies of melting of pure Ag and Cu from Ref. [9]. Such negative values correspond to strong short-range order in the melts in agreement with their negative enthalpies of formation [1,2].

In the temperature range investigated just above their melting points, the linear dependences on temperature of the enthalpies of both liquid eutectics lead to constant heat capacities as for many pure liquid metals. There is no drastic change of structure when temperature increases in contrast with the case of the Te-rich Ge–Te eutectic [4]. The enthalpies of mixing of the two systems investigated show strong minima [1,2] whose locations correspond to their congruently melting compounds ($Ag_2Te$ and $Cu_2Te$) and the behaviour of both binaries has been explained already in a very simple way by the existence of some $Ag_2Te$ and $Cu_2Te$ species. The two eutectics investigated here do not show any additional short-range order and can be considered as reference systems for our further works on weakly and moderately associated alloys.

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