

# DIFFERENCES IN PARTIAL THERMODYNAMIC FUNCTIONS OF SOME SECTIONS OF SYSTEMS Tl-Ag-Te AND Tl-Sb-Te

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## Abstract

The EMF concentration cell method was applied to determine excess partial molar thermodynamic functions for some sections of the systems Tl-Ag-Te and Tl-Sb-Te. The presence of binary and ternary associates is assumed in Tl-Ag-Te solutions.

**Keywords:** thermodynamic functions, Tl-Ag-Te system, Tl-Sb-Te system

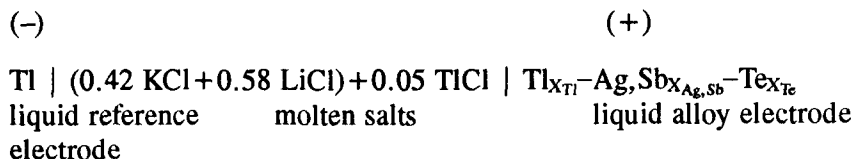
## Introduction

Ternary metallic solutions containing tellurium belong among the less-known systems as regards their thermodynamic properties. In most cases, the components of these solutions form numerous ternary compounds.

The main topic of the present communication is a comparison of the thermodynamic excess partial functions of thallium for two chosen sections of the systems Tl-Sb-Te and Tl-Ag-Te. Both systems were investigated by means of the EMF concentration cell method.

## Experimental

The following cells were constructed:



The reference electrodes were prepared from 99.98% pure thallium (POCh) and the alloy electrodes from the same thallium, electrolytically refined silver, 99.98% pure antimony (Aldrich) and 99.98% pure tellurium (POCh). The tellurium was melted before use under a layer of molten salt mixture (0.58 LiCl + 0.42 KCl) to remove traces of  $\text{TeO}_2$ . The construction of the cell and the measurement technique were described earlier [1]. The concentration cell EMF measurements [ $E$ ] started about 12 h after the cell was assembled and filled with argon, using an E-541 Meratronik voltmeter. Each series of measurements lasted up to one week.

## Results and discussion

The electromotive force ( $E$ ) and its temperature coefficients for liquid Tl-Sb-Te solutions were determined from the sections  $X_{\text{Sb}}:X_{\text{Te}}=1:4$  and 1:1.

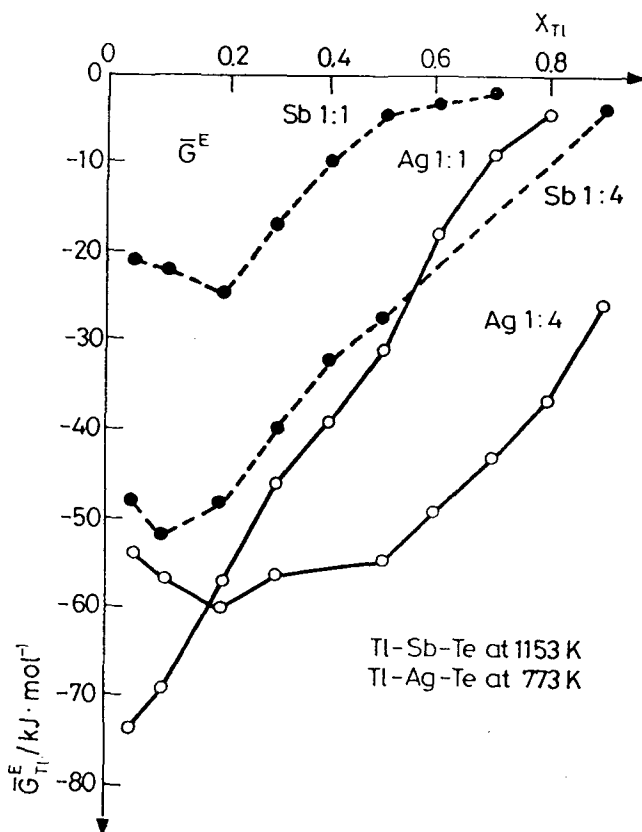


Fig. 1

The linear dependence of  $E$  vs. temperature,  $E=f(T)$ , was obtained for 8 alloys relating to the section  $X_{\text{Sb}}:X_{\text{Te}}=1:4$  in the concentration range  $X_{\text{Tl}}=0.050-0.700$  and for 8 alloys for the section  $X_{\text{Sb}}:X_{\text{Te}}=1:1$  and the concentration range  $X_{\text{Tl}}=0.050-0.800$ . The measurements were made in the temperature range 1053–1163 K.

The Tl-Ag-Te solutions were also studied along the same sections  $X_{\text{Ag}}:X_{\text{Te}}=1:4$  and 1:1, in the concentration range  $X_{\text{Tl}}=0.050-0.900$  and in the temperature range 723–887 K. Here too, the linear dependence  $E=f(T)$  was observed for all constructed galvanic cells. Although the temperature ranges of measurements were different, it seems acceptable to compare the calculated excess partial molar thermodynamic values of thallium for both sections of both investigated systems.

Figure 1 presents the excess partial molar free enthalpies  $G_{\text{Tl}}^E$  of thallium for the system Tl-Sb-Te, calculated at 1153 K, and that for the system Tl-Ag-Te at 773 K. The excess partial free enthalpy is more negative for solutions in the system Tl-Ag-Te than for Tl-Sb-Te alloys. Further,  $G_{\text{Tl}}^E$  for  $X_{\text{Ag,Sb}}:X_{\text{Te}}=1:1$  is less negative than for  $X_{\text{Ag,Sb}}:X_{\text{Te}}=1:4$ .

Figure 2 presents the excess partial molar entropies of thallium,  $S_{\text{Tl}}^E$ . In contrast with the  $G_{\text{Tl}}^E$  values, the curves of the partial molar entropies of thallium differ from one another. The curves of the excess partial molar entropies of thallium show maxima situated at a concentration of nearly  $X_{\text{Tl}}\approx 0.40$  for both sections of the system Tl-Sb-Te. The  $S_{\text{Tl}}^E$  values for both sections of the system Tl-Sb-Te are positive, while those for the system Tl-Ag-Te, and especially for  $X_{\text{Ag}}:X_{\text{Te}}=1:4$ , decline monotonously from positive to negative values. For the section  $X_{\text{Ag}}:X_{\text{Te}}=1:1$ , the initial decrease in  $S_{\text{Tl}}^E$  is even more accentuated, but at  $X_{\text{Tl}}\approx 0.50$  an increase is observed up to values close to zero.

Figure 3 gives the partial molar enthalpies of thallium,  $\Delta\bar{H}_{\text{Tl}}$ , for both investigated systems. A characteristic maximum in the  $\Delta\bar{H}_{\text{Tl}}$  values appears for the section  $X_{\text{Sb}}:X_{\text{Te}}=1:4$  for Tl-Sb-Te at  $X_{\text{Tl}}\sim 0.70$ , and for the section  $X_{\text{Sb}}:X_{\text{Te}}=1:1$  at  $X_{\text{Tl}}\sim 0.40$ . The  $\Delta\bar{H}_{\text{Tl}}$  values for Tl-Sb-Te alloys are positive in a considerable thallium concentration range, while the corresponding values for the system Tl-Ag-Te are negative in the whole concentration range, though with increase of the thallium content in the alloy the absolute values of  $\Delta\bar{H}_{\text{Tl}}$  decrease.

The course of the partial excess molar thermodynamic functions usually depends on the phase diagram, the number of compounds formed, their stability, the chemical bonding between the components and the size and valency of the elements in the system.

The ternary systems Tl-Sb-Te and Tl-Ag-Te have one common boundary binary system, Tl-Te. Thallium and tellurium form two incongruently melting

compounds,  $Tl_2Te_3$  and  $TlTe$ , and two congruently melting ones,  $Tl_5Te_3$  and  $Tl_2Te$ . In fact,  $Tl_5Te_3$  is an intermediate phase existing in the concentration range  $0.620 \leq X_{Tl} \leq 0.640$  [2]. The phase diagrams of the systems Ag-Tl and Sb-Tl are of eutectic type [3], while the components of the systems Sb-Te and Ag-Te form stable compounds. In the system Sb-Te, one compound is formed,  $Sb_2Te_3$ , melting congruently at 895 K [4].  $Sb_2Te_3$  is a *p*-type semiconductor crystallizing in the tetradymite type of rhombohedral crystal lattice. The atoms in such a crystal lattice are situated in layers arranged according to the scheme  $Te^1-Sb-Te^2-Sb-Te^1$ . In such a crystal lattice, all atoms situated in one layer are equal, and hence covalent bonding prevails between the antimony and tellurium.

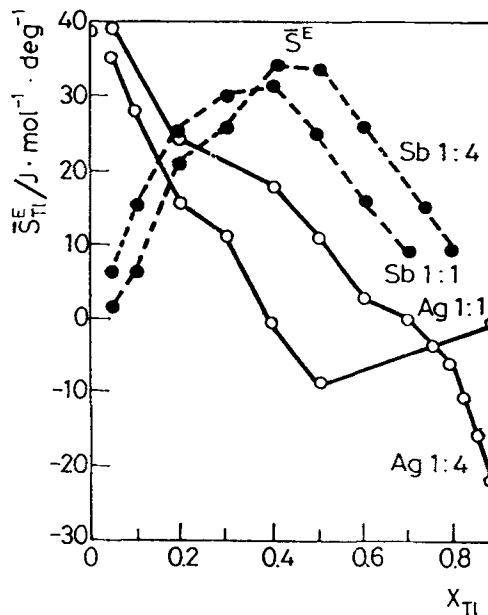


Fig. 2

In the system Ag-Te, three solid phase are formed:  $Ag_{5-x}Te_3$ , a  $\gamma$ -phase of variable composition, and  $Ag_2Te$ , melting congruently with a sharp maximum at 1233 K [5].

The existing information indicates that the numbers of ternary compounds in the systems Tl-Sb-Te and Tl-Ag-Te differ considerably. In the system Tl-Sb-Te, two compounds are formed,  $TlSbTe_2$  and  $Tl_9SbTe_6$  both in the section  $Tl_2Te-Sb_2Te_3$  [6, 7].

The number of ternary compounds known in the system Tl-Ag-Te is increasing constantly. Babanly and Kuliev reported five compounds in that sys-

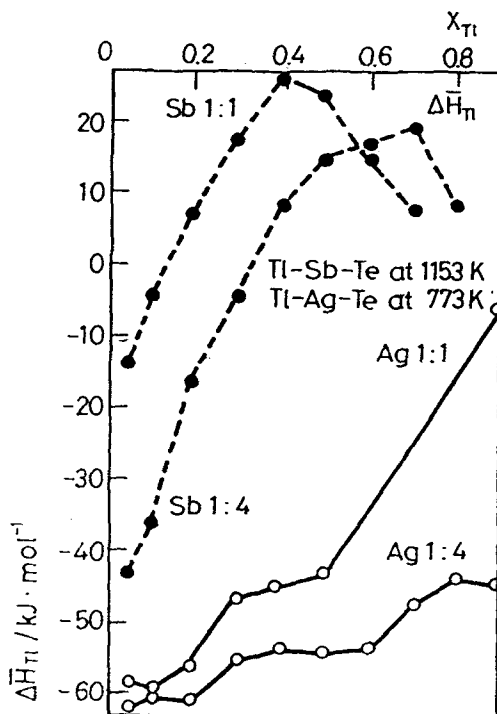


Fig. 3

tem:  $\text{AgTlTe}$ ,  $\text{Ag}_9\text{TlTe}_5$ ,  $\text{AgTlTe}_2$ ,  $\text{AgTl}_2\text{Te}_5$  and  $\text{AgTl}_3\text{Te}_2$  [8]. Investigations of the pseudobinary system  $\text{Tl}_2\text{Te}-\text{Ag}_2\text{Te}$  have raised questions concerning the formulae of the last two of these compounds. New stoichiometric compositions have been proposed:  $\text{Ag}_5\text{Tl}_9\text{Te}_7$  and  $\text{Ag}_4\text{Tl}_2\text{Te}_3$  [9]. Recent evidence [10, 11] points to additional ternary compounds in the system Tl-Ag-Te:  $\text{Ag}_{16}\text{Tl}_2\text{Te}_{11}$ ,  $\text{Ag}_{24-x}\text{Tl}_4\text{Te}_{15-y}$ , where  $x=2$  and  $y=0.1$ ,  $\text{Ag}_8\text{Tl}_2\text{Te}_5$  and  $\text{Ag}_{18}\text{Tl}_4\text{Te}_{11}$ .

It follows from X-ray studies that the distances between the Ag and Te atoms vary in the range 2.8–3.2 Å, which makes it difficult to decide whether the bond is covalent (according to Van Vechten-Philips 2.8 Å) or ionic (according to Shannon 3.2 Å). The Tl-Te and Te-Ag distances are longer than 3.4 Å, which is characteristic of ionic bonding.

The excess partial molar functions  $\bar{G}_{\text{Tl}}^E$  and  $\Delta\bar{H}_{\text{Tl}}$  for the system Tl-Ag-Te are more negative than those for the system Tl-Sb-Te, but it should be stressed that the molar enthalpy of mixing of Ag-Te solutions is much higher than that for Sb-Te solutions (-20.75 kJ/mol [12] and -9.6 kJ/mol [13], respectively). Both values were obtained for the solution concentration which corresponds to the most stable compound in the system,  $\text{Ag}_2\text{Te}$  and  $\text{Sb}_2\text{Te}_3$ , respectively. The differences in bond character between silver or antimony and tellurium are un-

doubtedly responsible for the higher negative  $\Delta\bar{H}_{\text{Tl}}$ , and  $\bar{G}_{\text{Tl}}^{\text{E}}$  values for the system Tl-Ag-Te than for the system Tl-Sb-Te.

It seems reasonable to believe that in the system Tl-Ag-Te the contribution of ionic bonding is higher than that in the system Ag-Te, which in consequence leads to a higher number of ternary compounds than the number in the system Tl-Sb-Te. This fact also leads to the negative values of the excess partial molar entropies of thallium in the system Tl-Ag-Te in the whole concentration range, whereas for the system Tl-Sb-Te the course of  $\bar{S}_{\text{Tl}}^{\text{E}}$  varies considerably: at lower thallium concentrations  $\bar{S}_{\text{Tl}}^{\text{E}}$  is positive, and with increasing thallium content it becomes negative.

These differences in course of the  $\bar{S}_{\text{Tl}}^{\text{E}}$  values can presumably be explained by the presence of various ternary or binary associates, such as the most stable compounds TlAgTe, Ag<sub>2</sub>Te, Tl<sub>2</sub>Te and possibly Tl<sub>5</sub>Te<sub>3</sub> + Tl in liquid Tl-Ag-Te. At the same time, the positive  $\bar{S}_{\text{Tl}}^{\text{E}}$  and  $\Delta\bar{H}_{\text{Tl}}$  values point to the lack of stable associates in Tl-Sb-Te solutions.

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**Zusammenfassung** — Die EMF Konzentrationszellenmethode wurde zur Bestimmung thermodynamischer partieller molarer Überschußfunktionen für einige Bereiche des Tl-Ag-Te und des Tl-Sb-Te-Systemes angewendet. In Tl-Ag-Te-Lösungen wird die Existenz von binären und ternären Assoziaten angenommen.