

## THERMODYNAMIC PROPERTIES OF $\text{CuSb}_2\text{O}_6$

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For the  $S_{298.15\text{ K}}^\circ$  standard entropy of the  $\text{CuSb}_2\text{O}_6$  *trirutile* type compound a value of 155.06

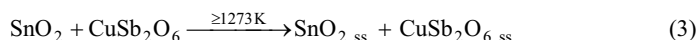
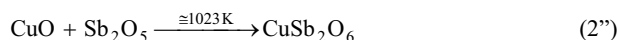
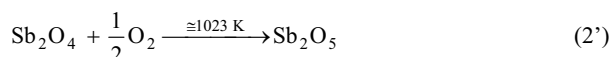
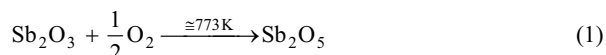
J/mole-K was calculated. The corresponding value of  $\Delta G_{298.15\text{ K, CuSb}_2\text{O}_6}^\circ = -1224.79$  kJ/mol was obtained, which agrees in reasonable limits with the reported data for  $\text{NiSb}_2\text{O}_6$  ( $\Delta_f G_{298.15}^\circ = -1245.514$  kJ/mol). The small magnitude of the calculated values seems to support the idea that CuO forms a much more stable compound with  $\text{Sb}_2\text{O}_5$  than with  $\text{Sb}_2\text{O}_3$ .

### Introduction

Thermodynamic data for  $\text{CuSb}_2\text{O}_6$  are of particular interest in determining the conditions under which the solid solutions in  $\text{SnO}_2$  -  $\text{Sb}_2\text{O}_3$  - CuO ternary system are formed [1,2], and may condition their relative stability to the initial components.

$\text{SnO}_2$  -  $\text{Sb}_2\text{O}_3$  - CuO compositions are technologically interesting because of their electrical [1÷3], catalytic [4] and gas-sensing properties [5].

Subsolidus phase relationships in the  $\text{SnO}_2$  -  $\text{Sb}_2\text{O}_3$  - CuO ternary system were extensively studied in our research group [6÷8]. These previous studies pointed out the complexity of the solid-state reactions in the CuO -  $\text{Sb}_2\text{O}_3$  binary system extending over the ternary phase formation ( $\text{SnO}_2$  ss and  $\text{CuSb}_2\text{O}_6$  ss solid solutions), as follows



In our studies [6], in agreement with the data published by Nakua [9], the copper antimony oxide was found to adopt a monoclinically distorted *trirutile* structure (space group  $\text{P}2_1/\text{n}$  with  $a_0=4.6349$  Å,  $c_0=9.2931$  Å,  $\beta=91.124^\circ$ ). The only supplementary information on this ternary oxide compound refers to its short range and long-range magnetic ordering [9], due to the presence of magnetic  $\text{Cu}^{2+}$  ion and its tendency to adopt a tetragonally elongated octahedral geometry.

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According to reaction (2'') and (3), the formation of  $\text{CuSb}_2\text{O}_6$  binary compound plays a defining role, being an intermediary step in the formation mechanism of  $\text{SnO}_2$  based solid solutions [6,7], with *rutile* type structure.

That is why, the main purpose of the present assessment was to provide a set of thermodynamic parameters giving a self - consistent description of the copper antimony oxide and to emphasize possible features regarding its stability at high temperatures.

## Experimental

The corresponding mixture for  $\text{CuSb}_2\text{O}_6$  binary compound was prepared by the classical ceramic method [8] using commercially available  $\text{Sb}_2\text{O}_3$  and  $\text{CuO}$  (Merck Co.), the stable oxides in standard conditions. The thermal stability of the obtained mixture was studied from room temperature up to 1273 K by DTA/TG measurements using a Perkin Elmer Instrument - Pyris 7 Differential Thermal Analyzer. For each sample the platinum reference pan was loaded with an amount of alumina powder equal to the weight of the powder in the sample pan. All DTA tests were performed with heating rates of 7 °C/min and natural cooling rates, in *air*.

## Standard Entropy $S_{298.15\text{ K}}^0$

Since the low-temperature heat capacity of  $\text{CuSb}_2\text{O}_6$  has not been measured yet, an exact value for its standard entropy at 298.15 K is not available.

However, by means of the empirical rule proposed by Latimer [10], this thermodynamic function can be evaluated as a sum of constants characteristic of the elements from which  $\text{CuSb}_2\text{O}_6$  is composed. For this purpose, the data presented in Table 1 have been used for calculating the corresponding  $S_{298.15\text{ K}}^0$  for  $\text{CuSb}_2\text{O}_6$ .

**Table 1. Entropy contribution in solid compounds of the elements at 298.15 K (cal/grd-mol)**

Element	Cu	Sb	O
$S^0$	7.97	10.5	24.502
Ref.	[11,12]	[11,12]	[11,12]

The calculated value of 242.94 J/mol·K for  $S_{298.15\text{ K}}^0$ , being of the same order of magnitude as the standard molal entropies of some oxides in vaporous state [13], it is somehow obvious that the obtained value is super - evaluated, and cannot be considered in further calculation. This is probably due to the fact that, neither the type of interaction between the  $\text{Cu}^{2+}$  and  $\text{Sb}^{5+}$  cations and  $\text{O}^{2-}$  anions, nor the energy levels corresponding to the various ways in which the structural units of  $\text{CuSb}_2\text{O}_6$  could be distributed, were considered.

However in estimating the molar entropy of a solid, it is a common procedure [10] to choose an analogous compound with a known entropy value, rather than compute  $S_{298.15\text{ K}}^0$  directly from the individual contributions of the elements.

Accordingly, based on the published heat capacity data for the isomorphous *tapiolite* compound  $\text{FeTa}_2\text{O}_6$  (Fig. 1) and the equation for defining the entropy content

$S_{298.15}^0 = S_{(0)} + \int_0^{298.15} C_p \frac{dT}{T}$ , we obtained a corresponding value of 155.0688 J/mole·K for  $\text{CuSb}_2\text{O}_6$ .

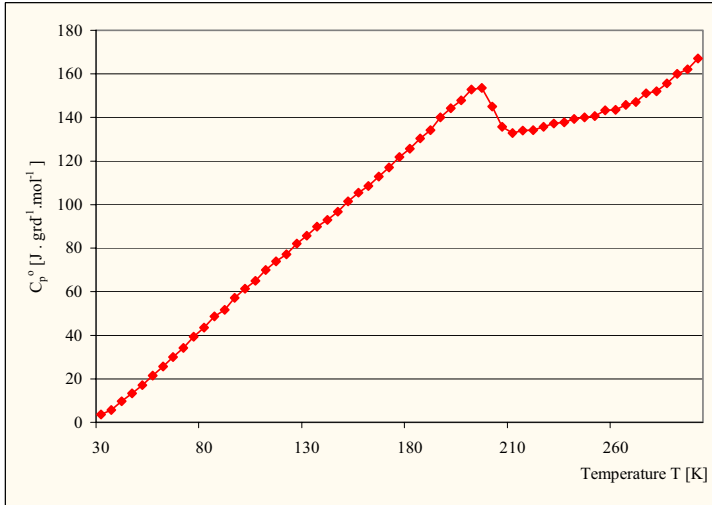


Fig. 1: Specific heat at constant pressure of  $\text{FeTa}_2\text{O}_6$ ,  $C_p^0 = f(T)$ ; data from ref. [14].

### Enthalpy of Formation $\Delta H_{298.15 \text{ K}}^0$

The enthalpy of formation of  $\text{CuSb}_2\text{O}_6$  has not been measured so far. It can be approximated by taking into consideration its formation from binary oxides [15].

According to our previous reported results [16,17], when heating an equimolar mixture of  $\text{CuO}$  and  $\text{Sb}_2\text{O}_3$  one may notice on the resulting DTA curve (Fig. 2) the 764 K thermal effect assigned to reaction (1).

On the contrary, for the reactions (2') and (2'') no thermal effects either exo- or endothermic have been observed on the DTA curve. However, copper antimony oxide was the only phase identified by XRD for the equimolar mixture heated in non - isothermal conditions [2] up to 1273 K.

Consequently, the present thermodynamic calculation was done under the assumption that the heat amount released due to reaction (2') has been consumed for balancing the enthalpy change of reaction (2'') accompanying the formation of  $\text{CuSb}_2\text{O}_6$ .

The enthalpy change due to reaction (2') reported in the literature [18] has been used as a numerical value for the reaction (2'').

The obtained standard enthalpies and entropies of formation calculated for  $\text{CuSb}_2\text{O}_6$  under the mentioned above assumption, relative to the component elements and component binary oxides are presented in Table 2.

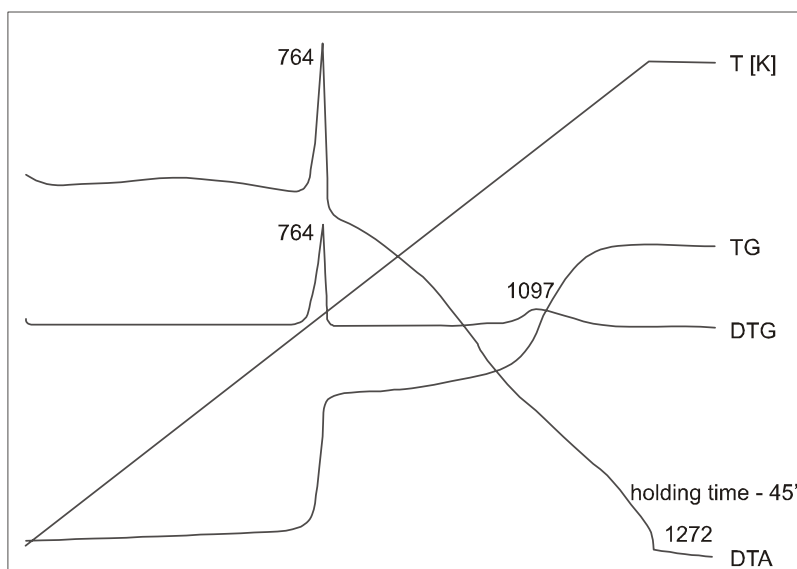


Fig. 2: DTA/TG results for a mixture with  $\text{CuO}:\text{Sb}_2\text{O}_3 = 1:1$ ; air, 7 grd / min.

Usually, all the enthalpies of formation for the ternary oxide compounds of the  $\text{AB}_x\text{O}_y$  type are in the range of 0 kJ/mol to  $-300$  kJ/mol, the stabilisation of the ternary compounds being generally considerably less in magnitude than the formation enthalpies of its component binary oxides.

The obtained value for  $\text{CuSb}_2\text{O}_6$  of  $-85.3536$  kJ/mol (Table 2), is placed approximately within the first one third of the above mentioned interval, in the less negative portion of that range, indicating that the stability of  $\text{CuSb}_2\text{O}_6$  derives from its entropy (configurational and / or vibrational) not from its change in the enthalpy of formation.

Table 2. Thermodynamic properties of  $\text{CuSb}_2\text{O}_6$  and its components at 298.15K

Compound	$\Delta_{f(\text{ox})}H_{298.15}^{\circ}$ kJ/mol	$\Delta_f H_{298.15}^{\circ}$ kJ/mol	$\Delta_{f(\text{ox})}S_{298.15}^{\circ}$ J/mol-K	$\Delta_f S_{298.15}^{\circ}$ J/mol-K	$S_{298.15}^{\circ}$ J/mol-K	Reference
Sb	-	-	-	-	45.52	18
Cu	-	-	-	-	33.15	18
CuO	-	-156.06	-	-	42.590	18
$\text{Sb}_2\text{O}_3$	-	-692.03	-	-	-	18
$\text{Sb}_2\text{O}_4$	-	-891.192	-	-	-	18
$\text{Sb}_2\text{O}_5$	-	-962.32	-	-	125.10	18
$\text{O}_2$	-	-	-	-	205.02	18
$\text{CuSb}_2\text{O}_6$	-85.3536	-1050.602	-12.63	-584.18	155.07	this study

### Free Energy of Formation $\Delta G_{298.15\text{ K}}^0$

By conventional third - law analysis of the data, the values obtained in this study for both  $\Delta_f H_{298.15}^0$  ( $\text{CuSb}_2\text{O}_6$ ) and  $\Delta_f S_{298.15}^0$  ( $\text{CuSb}_2\text{O}_6$ ) presented in Table 2 allow the calculation of the free Gibbs energy of formation

$$\Delta G_{298.15\text{ K}}^0(\text{CuSb}_2\text{O}_6) = \Delta H_{298.15\text{ K}}^0(\text{CuSb}_2\text{O}_6) - T \cdot \Delta S_{298.15\text{ K}}^0(\text{CuSb}_2\text{O}_6) = -1224.79\text{ kJ/mol.}$$

Nevertheless, there is no published thermodynamic information in the literature about the copper antimony oxides against which the values obtained in this study may be compared. However, the value of  $\Delta G_{298.15\text{ K}}^0(\text{CuSb}_2\text{O}_6) = -1224.79\text{ kJ/mol}$  obtained in the present work, agrees in reasonable limits with the reported data for the isomorphous compound  $\text{NiSb}_2\text{O}_6$ , ( $\Delta_f G_{298.15}^0 = -1245.514\text{ kJ/mol}$ ) [19] assessed by computing the entropy change for the solid-solid reactions.

### Conclusion

As a general conclusion, the small magnitude of the values calculated for  $\text{CuSb}_2\text{O}_6$ , relative to the component oxides compared to the standard conditions (i. e. to the elements) indicates that  $\text{CuO}$  forms a much more stable compound with  $\text{Sb}_2\text{O}_5$  than with  $\text{Sb}_2\text{O}_3$ . Since its stability derives from structural reasons (entropy content) as was explained before, it can be concluded that at low temperature  $\text{CuSb}_2\text{O}_6$  probably presents the tendency to be metastable relative to  $\text{CuO}$  and  $\text{Sb}_2\text{O}_5$  [20].

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