

# BEHAVIOR OF COPPER CHALCOGENIDES DURING VACUUM-THERMAL PROCESSING

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Preliminary Note – Prethodno priopćenje

In this work, thermodynamic functions of evaporation of copper chalcogenides ( $\text{Cu}_2\text{S}$ ,  $\text{Cu}_2\text{Se}$ , and  $\text{Cu}_2\text{Te}$ ) are determined via previously published data and thermodynamic values obtained by the authors of the work. The obtained results indicate a very low probability of separation of compounds into copper and chalcogen by dissociation under vacuum-thermal processing conditions. Liquid-vapor phase transitions in binary systems  $\text{Cu}_2\text{S} - \text{Cu}_2\text{Se}$ ,  $\text{Cu}_2\text{S} - \text{Cu}_2\text{Te}$ , and  $\text{Cu}_2\text{Se} - \text{Cu}_2\text{Te}$  at low pressures of 15 and 0,7 kPa are constructed based on the vapor pressure of copper chalcogenides. It is shown that the pressure eases over the liquid bath impairs the separation of chalcogens, therefore separation in one stage by thermo-vacuum treatment at a pressure of 0,7 – 15 kPa is not possible.

*Keywords:* copper chalcogenides; vacuum; thermal processing; dissociation; vapor pressure

## INTRODUCTION

Copper chalcogenides form the basis of the mattes of copper and lead plants.

Electrorefining of copper produces a multicomponent product – copper-electrolyte slime, which containing chalcogens in the form of their compounds with copper, silver, and gold. The slime is used as a raw material for production of noble metals', selenium and tellurium. One of the valuable products of copper refining is its telluride, which includes impurities of other elements and compounds.

Review papers [1-3] summarize information on the technologies developed over the last 30 years. It can be concluded from the analyzed data that the interest of researchers is aimed at the development of hydrometallurgical schemes, which are not perfect and are characterized by multistage. Therefore, the development of a cost-effective and environmentally friendly method is of great importance for the industry.

It is of interest to consider thermodynamic properties of copper chalcogenides and double systems with their participation in terms of determining the boundaries of vapor-liquid equilibrium, the possibility of dissociative extraction of chalcogens from compounds, the distribution of elements, and their concentration in an individual middling product.

Data on the saturated vapor pressure of liquid  $\text{Cu}_2\text{S}$ ,  $\text{Cu}_2\text{Se}$ , and  $\text{Cu}_2\text{Te}$  are needed to determine the boundaries of the liquid and vapor phase coexistence fields.

Information concerning  $\text{Cu}_2\text{S}$  is summarized in monographs [4, 5], where only the dissociation pressure

values of the liquid compound are given. The dissociation pressure of crystalline  $\text{Cu}_2\text{Se}$  and  $\text{Cu}_2\text{Te}$  is given in studies [6, 7]. The chalcogens activities in liquid copper for temperatures 1 150 – 1 500 °C were determined in [8] for small contents of sulfur (1,97 – 3,66 at. %), selenium (1,5 – 2,7 at. %) and tellurium (2,32 – 4,31 at. %), are insufficient for calculation of partial pressures of components.

Values of the saturated vapor pressure of copper chalcogenides above their melting point were calculated in this work. They were determined as the sum of the partial pressures of the components. Available data on the dissociation pressure of compounds, values of the saturated vapor pressure of the elements, thermodynamic functions available in the reference literature, and properties of similarity were used in the calculations.

## VAPOR PRESSURE OVER COPPER SULFIDE MELT

The dissociation pressure of copper sulfide determined for the temperature range 1 200 – 1 400 °C and recommended by the authors [4] for calculations is converted to the form:  $\ln p_s = 25,869 - 36\,484 \cdot T^{-1}$  Herein after:  $p$  – pressure / Pa;  $T$  – temperature / K. Melting point of  $\text{Cu}_2\text{S}$  is 1 130 °C [9]. Complete dissociative decomposition of copper sulfide into copper and sulfur is possible, based on the dissociation pressure value, at 2 271 °C, which is not possible under industrial conditions.

The activity of an element can be defined as the ratio of the partial pressure over the melt, in this case, the dissociation pressure, to the vapor pressure over the pure element. We have determined the sulfur activity for the melt, the composition of which corresponds to

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the stoichiometry of  $\text{Cu}_2\text{S}$ . The vapor pressure of elemental sulfur above the boiling point – 429 °C [10] is determined according to Charles's law [11], and, in the absence of data for sulfur, the thermal pressure coefficient is taken as the average for 12 gases available in the reference book [12] and differing in the fourth decimal point equal to 0,00367 deg<sup>-1</sup>. Then the copper activity coefficient and the activity for the composition  $\text{Cu}_2\text{S}$  were found by integrating the Gibbs-Duhem equation. The calculation was performed for 1 300 °C, and the activity coefficients were assumed to be independent of temperature. The activity of copper in a melt with sulfur for the composition of the compound under these conditions was 0,1586.

The vapor pressure over liquid metallic copper according to [13] is represented in the form of the equation:

$$\ln p_{\text{Cu}(l)} = 24,957 - 37\,926 \cdot T^{-1}.$$

In [14], the vapor pressure of liquid copper is represented by three equations transformed to the form:

$$\ln p_{\text{Cu}(l)} = 24,308 - 36\,659 \cdot T^{-1},$$

$$\ln p_{\text{Cu}(l)} = 24,379 - 36\,606 \cdot T^{-1},$$

$$\ln p_{\text{Cu}(l)} = 24,389 - 36\,609 \cdot T^{-1}.$$

The values of the partial vapor pressure of copper over the liquid compound were obtained by multiplying the averaged value of vapor pressure over pure copper by its activity, and summing up with the partial pressure of sulfur - the total vapor pressure over molten  $\text{Cu}_2\text{S}$ , expressed by the dependence:

$$\ln p_{\text{Cu}_2\text{S}(l)} = 25,908 - 36\,511 \cdot T^{-1}.$$

The contribution of the value of the vapor pressure of liquid copper to the total vapor pressure over molten sulfide according to [13] was 0,87 %, and according to [14] was 2,88 ÷ 3,23 %, which is within the error of the experiments to determine the dissociation pressure of the compound.

The thermodynamic functions of evaporation of  $\text{Cu}_2\text{S}$  are  $\Delta H_{\text{Cu}_2\text{S}(l)}^{\text{evap.}} = 303,6$  kJ/mol and  $\Delta S_{\text{Cu}_2\text{S}(l)}^{\text{evap.}} = 119,58$  J/(mol · K).

## VAPOR PRESSURE OVER MOLTEN COPPER TELLURIDE

The vapor pressure of tellurium over solid copper telluride  $\text{Cu}_2\text{Te}$  is given in studies [5, 7], and we have transformed it to the form  $\ln p_{\text{Te}} = 21,062 - 28\,393 \cdot T^{-1}$ . Hence, the decomposition of the compound into copper and tellurium is possible only above 2 704 °C.

Tellurium boiling point we determined earlier [15] from the vapor pressure equation over the pure element is.  $\ln p_{\text{Te}}^0 = 24,797 - 12\,540 \cdot T^{-1}$ , which is 989 °C. The vapor pressure Te corresponds to the dependence  $\ln p_{\text{Te}}^0 = 371,87 \cdot T - 367\,969$ , above the boiling point of tellurium to the melting point of copper (1 083 °C).

The total pressure over crystalline copper telluride is taken as the equation:  $\ln p_{\text{Cu}_2\text{Te}} = 21,062 - 28\,393 \cdot T^{-1}$  due to the vanishingly small partial pressure of copper at these temperatures  $(8,5 - 9,5) \cdot 10^{-12} \div (5,5 - 6,2) \cdot 10^{-10}$ . The determined entropy of sublimation  $\Delta S_{\text{Cu}_2\text{Te}(cryst.)}^{\text{subl.}} = 79,3$  J/(mol · K) and the enthalpy  $\Delta H_{\text{Cu}_2\text{Te}(cryst.)}^{\text{subl.}} = 236,1$  kJ/mol.

The enthalpy of vaporization of a liquid compound can be defined as:  $\Delta H^{\text{evap.}} = \Delta H^{\text{subl.}} - \Delta H^{\text{melting}}$ , but there are no data on the melting heat of copper telluride in our case. The reference book [10] gives similar melting functions for  $\text{Cu}_2\text{S} - 11,3$  kJ/mol and  $\text{Cu}_2\text{Se} - 18,0$  kJ/mol. The latter is calculated to be 24,7 kJ/mol, assuming the linear dependence of the enthalpy of melting on the atomic number (as is the case for the enthalpy of formation of  $\text{Cu}_2\text{S}$ ,  $\text{Cu}_2\text{Se}$ , and  $\text{Cu}_2\text{Te}$ ).

At the same time, it is known that the dependence of the vapor pressure in the coordinates  $\ln p_i - T^{-1}$  above crystalline and liquid samples has a break at the melting point of the solid phase and, accordingly, equal values of vapor pressure. The temperature dependence of the pressure of liquid copper telluride, corresponding to the expression:  $\ln p_{\text{Cu}_2\text{Te}(l)} = 18,939 - 25\,426 \cdot T^{-1}$  is found, by jointly solving the equations of vapor pressure dependence for the crystal and liquid phases at the transition temperature crystal → liquid (1 125 °C) and converting the value of  $\Delta H_{\text{Cu}_2\text{Te}(l)}^{\text{evap.}}$  into the coefficient of the Arrhenius equation.

The thermodynamic functions of evaporation of  $\text{Cu}_2\text{Te}$ :  $\Delta H_{\text{Cu}_2\text{Te}(l)}^{\text{evap.}} = 211,4$  kJ/mol and  $\Delta S_{\text{Cu}_2\text{Te}(l)}^{\text{evap.}} = 62,63$  J/(mol · K).

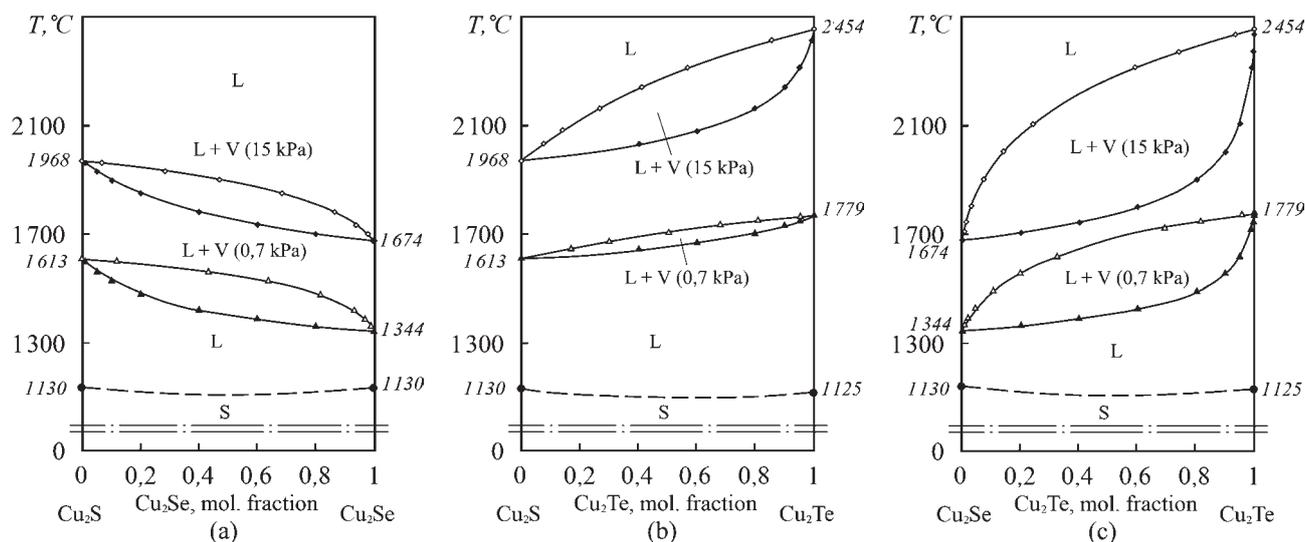
## VAPOR PRESSURE OVER COPPER SELENIDE MELT

The vapor pressure of selenium over crystalline  $\text{Cu}_2\text{Se}$  is given in the study [7] and converted to:  $\ln p_{\text{Se}} = 24,644 - 29\,258 \cdot T^{-1}$ . The saturated vapor pressure over molten  $\text{Cu}_2\text{Se}$  is calculated similarly to that over liquid  $\text{Cu}_2\text{Te}$  and corresponds to  $\ln p_{\text{Cu}_2\text{Se}(l)} = 24,644 - 29\,258 \cdot T^{-1}$ . The equilibrium temperature of the dissociation reaction of copper selenide into selenium and copper corresponds to 1 957 °C, which is significantly higher than the temperatures of technological processes of extraction by the pyrometallurgical method.

The enthalpy and entropy of evaporation are respectively equal:  $\Delta H_{\text{Cu}_2\text{Se}(l)}^{\text{evap.}} = 62,63$  kJ/mol and  $\Delta S_{\text{Cu}_2\text{Se}(l)}^{\text{evap.}} = 109,06$  J/(mol · K).

## THE SYSTEMS OF $\text{Cu}_2\text{S}-\text{Cu}_2\text{Se}$ , $\text{Cu}_2\text{S}-\text{Cu}_2\text{Te}$ AND $\text{Cu}_2\text{Se}-\text{Cu}_2\text{Te}$

Determination of vapor pressure values by mass spectrometry over crystal systems  $\text{Cu}_2\text{S} - \text{Cu}_2\text{Te}$  at 999 – 1 170 K (726 – 897 °C) and  $\text{Cu}_2\text{Se} - \text{Cu}_2\text{Te}$  at 954 – 1 257 K (681 – 984 °C) in the entire concentration range was performed by a team of authors [14, 15]. The predomi-



**Figure 1** Fields of vapor-liquid equilibrium in double chalcogenide systems of copper in a vacuum: (a)  $\text{Cu}_2\text{S}$ - $\text{Cu}_2\text{Se}$ ; (b)  $\text{Cu}_2\text{S}$ - $\text{Cu}_2\text{Te}$ ; (c)  $\text{Cu}_2\text{Se}$ - $\text{Cu}_2\text{Te}$

nant amount of  $\text{Te}_2$  dimers was found in the vapor phase, for alloys containing more than 80 mol. %  $\text{Cu}_2\text{Se}$  – a certain number of  $\text{Se}_2$  molecules. Sulfur is found only at temperatures close to the melting of the compound. The authors explain this by the low sensitivity of the device.

A very significant sign-variable change in the activity of  $\text{Cu}_2\text{Te}$  in both systems was found. Moreover, the activity in the  $\text{Cu}_2\text{S}$ - $\text{Cu}_2\text{Te}$  system changes sign twice at 900 K (calculated by us), and it reaches a value of 1,23 at 60 mol. %  $\text{Cu}_2\text{Te}$ . In the same way, at 950 K ( $\text{Cu}_2\text{S}$ - $\text{Cu}_2\text{Te}$ ) the activity of copper telluride at 20 mol. % in the alloy reaches a value of 1,43. This, apparently, is associated with methodological errors, since the partial pressure of the component over the solution cannot be greater than the value of the saturated vapor pressure over the pure compound.

At the same time, the change in the vapor pressure of chalcogenides satisfactorily corresponds to a linear relationship connecting the ordinates of the vapor pressure values of compounds, which allows us to consider the crystalline systems close to the ideal state within the error of the experiments indicated by the authors.

No studies devoted to the determination of the activity of melt components, as well as data for  $\text{Cu}_2\text{S}$ - $\text{Cu}_2\text{Se}$  melts have been found, however, by analogy with the  $\text{Cu}_2\text{S}$ - $\text{Cu}_2\text{Te}$  and  $\text{Cu}_2\text{Se}$ - $\text{Cu}_2\text{Te}$  systems, the named system is adopted corresponding to Raoult's law.

In this connection, the phase transitions for the above-molten systems are calculated according to the law of ideal solutions, as well as the fact that the system tends to the ideal state regardless of the sign of deviation as the temperature rises. Melt-vapor phase transitions at pressures corresponding to low-pressure distillation processes are shown in Figure 1. The melting temperature curves (dashed lines) are shown symbolically due to the lack of state diagrams.

Note that the constituents of the vapor will not be copper chalcogenides, but sulfur, selenium, and tellurium formed by the thermal dissociation of compounds.

In this case, the composition of the vapor phase for nonvolatile chalcogenides, which, in this case, are  $\text{Cu}_2\text{S}$ ,  $\text{Cu}_2\text{Se}$ , and  $\text{Cu}_2\text{Te}$ , found as the ratio of partial pressures, is conventionally indicated by the corresponding molar fractions of compounds.

$\text{Cu}_2\text{S}$  at a pressure of 0,7 kPa and a temperature above 1 613 °C,  $\text{Cu}_2\text{Se}$  above 1 344 °C,  $\text{Cu}_2\text{Te}$  above 1 779 °C can be completely decomposed into copper and the corresponding chalcogen under equilibrium conditions. It should be noted that the accuracy of the indicated temperatures depends on the error in determining the vapor pressure of the dissociation of compounds. However, the average temperature level indicates a very low probability of the separation of compounds into copper and chalcogen under the conditions of vacuum-thermal processing of matte melts and technical copper telluride.

It can be seen, when considering the position of the boundaries of the melt-vapor phase transitions, that a decrease in pressure above the liquid bath worsens the separation of chalcogens – the width of the fields of coexistence of liquid and vapor in temperature decreases. Tellurium ( $\text{Cu}_2\text{Te}$ ) has the lowest volatility, and selenium ( $\text{Cu}_2\text{Se}$ ) has the highest. Separation of chalcogens in one stage by thermo-vacuum treatment of mattes at a process pressure of 0,7 – 15 kPa is not possible.

The dissociation pressure of pure copper sulfide will range from 0,5 – 7 Pa, copper selenide 28 – 230 Pa, copper telluride 1,5 – 9 Pa in the process of low-pressure volatile distillation, as a rule, at temperatures of 1 100 – 1 250 °C. The formation of liquid solutions will lower the vapor pressure in proportion to the concentration of the constituents of the melt. Consequently, copper sulfide and telluride completely, and copper selenide – will be predominantly concentrated in the distillation residue.

## CONCLUSIONS

Thermodynamic functions of copper chalcogenide evaporation were determined based on published data

and thermodynamic values found by the authors. The entropies of vaporization of cuprous sulfide, selenide, and telluride were 119,6, 109,6, and 61,6 J/(mol·K), and the enthalpies were 303,6, 243,3, and 211,4 kJ/mol, respectively. The temperatures of complete dissociative decomposition for the indicated copper chalcogenides at atmospheric pressure are calculated to be 2 271 °C (Cu<sub>2</sub>S), 1 957 °C (Cu<sub>2</sub>Se) and 2 704 °C (Cu<sub>2</sub>Te), at 0,7 kPa – 1 613 °C (Cu<sub>2</sub>S), 1 344 °C (Cu<sub>2</sub>Se), and 1 779 °C (Cu<sub>2</sub>Te), which indicates a very low probability of separation of compounds into copper and chalcogen by dissociation under vacuum-thermal processing.

Liquid-vapor phase transitions in the Cu<sub>2</sub>S-Cu<sub>2</sub>Se, Cu<sub>2</sub>S-Cu<sub>2</sub>Te, and Cu<sub>2</sub>Se-Cu<sub>2</sub>Te double systems at low pressures of 15 and 0,7 kPa were constructed, based on the vapor pressure values of copper chalcogenides. It was found, when considering the position of the boundaries of the melt-vapor phase transitions, that a decrease in pressure above the liquid bath worsens the separation of chalcogens – the width of the fields of coexistence of liquid and vapor in temperature decreases. Cu<sub>2</sub>Te has the lowest volatility-total vapor pressure, and Cu<sub>2</sub>Se has the highest. Separation of chalcogens in one stage by thermo-vacuum treatment of matte at a process pressure of 0,7 – 15 kPa is not possible.

The dissociation pressure of pure copper sulfide will range from 0,5 to 7 Pa, copper selenide 28 – 230 Pa, copper telluride 1,5 – 9 Pa in the process of low-pressure volatile distillation, as a rule, at temperatures of 1 100 – 1 250 °C. The formation of liquid solutions will lower the vapor pressure in proportion to the concentration of the melt constituents. Consequently, copper sulfide and telluride completely, and copper selenide – mainly will be concentrated in the cube residue.

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**Note:** The responsible for English language is Alina Nitsenko, Almaty, Kazakhstan