In this work, thermodynamic functions of evaporation of copper chalcogenides (Cu₂S, Cu₂Se, and Cu₂Te) 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 Cu₂S – Cu₂Se, Cu₂S – Cu₂Te, and Cu₂Se – Cu₂Te 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 Cu₂S, Cu₂Se, and Cu₂Te are needed to determine the boundaries of the liquid and vapor phase coexistence fields.

Information concerning Cu₂S is summarized in monographs [4, 5], where only the dissociation pressure values of the liquid compound are given. The dissociation pressure of crystalline Cu₂Se and Cu₂Te 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: \( \ln p_S = 25,869 - 36,484 \cdot T^{-1} \). Hereinafter: \( p \) – pressure / Pa; \( T \) – temperature / K. Melting point of Cu₂S 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...
the stoichiometry of Cu₃S. 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⁻¹. Then the copper activity coefficient and the activity for the composition Cu₃S 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 Cu₃S, expressed by the dependence:

\[ \ln p_{\text{Cu₃S}(l)} = 25,908 - 36,511 \cdot T^{-1}. \]

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 Cu₃S are \( \Delta H_{\text{evap}}^{\text{Cu₃S}(l)} = 303.6 \text{ kJ/mol} \) and \( \Delta S_{\text{evap}}^{\text{Cu₃S}(l)} = 119.58 \text{ J/(mol} \cdot \text{K}) \).

### VAPOR PRESSURE OVER MOLTEN COPPER TELLURIDE

The vapor pressure of tellurium over solid copper telluride Cu₄Te is given in the study [5, 7] and converted to:

\[ \ln p_{\text{T}_{\text{eq}}} = 24,644 - 29,258 \cdot T^{-1}. \]

The saturated vapor pressure over molten Cu₄Te is calculated similarly to that over liquid Cu₄Te and corresponds to \( \ln p_{\text{Cu₄Te}(l)} = 24,644 - 29,258 \cdot T^{-1} \). The equilibrium temperature of the dissociation reaction of copper telluride into selenium and copper corresponds to 1 057 °C, which is significantly higher than the temperatures of technological processes of extraction by the pyrometallurgical method.

The enthalpy and entropy of evaporation of Cu₄Te:

\[ \Delta H_{\text{evap}}^{\text{Cu₄Te}(l)} = 211.4 \text{ kJ/mol} \] and \( \Delta S_{\text{evap}}^{\text{Cu₄Te}(l)} = 62.63 \text{ J/(mol} \cdot \text{K}) \).

### THE SYSTEMS OF Cu₃S-Cu₂Se, Cu₂S-Cu₂Te AND Cu₂Se-Cu₂Te

Determination of vapor pressure values by mass spectrometry over crystal systems Cu₃S – Cu₄Te at 999 – 1 170 K (726 – 897 °C) and Cu₂S – Cu₂Te at 954 – 1 257 K (681 – 984 °C) in the entire concentration range was performed by a team of authors [14, 15]. The predomi-
A significant amount of Te₂ dimers was found in the vapor phase, for alloys containing more than 80 mol. % Cu₂Se—a certain number of Se₂ 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 Cu₂Te in both systems was found. Moreover, the activity in the Cu₂S-Cu₂Te system changes sign twice at 900 K (calculated by us), and it reaches a value of 1.23 at 60 mol. % Cu₂Te. In the same way, at 950 K (Cu₂S-Cu₂Te) 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 Cu₂S, Cu₂Se, and Cu₂Te, found as the ratio of partial pressures, is conventionally indicated by the corresponding molar fractions of compounds.

Cu₂S at a pressure of 0.7 kPa and a temperature above 1613 °C, Cu₂Se above 1344 °C, Cu₂Te above 1779 °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 (Cu₂Te) has the lowest volatility, and selenium (Cu₂Se) 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 1100–1250 °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 (Cu₂S), 1,957 °C (Cu₂Se) and 2,704 °C (Cu₂Te), 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 Cu₂S-Cu₂Se, Cu₂S-Cu₂Te, and Cu₂Se-Cu₂Te 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. Cu₂Te has the lowest volatility-total vapor pressure, and Cu₂Se 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 1100 –1250 °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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REFERENCES


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