

### THERMODYNAMIC PROPERTIES OF Cu-S SOLUTIONS

A new method for description of thermodynamic properties of Cu-S mixtures is put forward. The basic feature of this method is the assumption that the activity coefficient of sulphur dissolved in liquid copper is equal to 1 for infinite dilute solution ( $\gamma_{[S]} = 1$  for  $x_{[S]} = 0$ ). In consequence the following relationships were established:

1. The equilibrium constant for the reaction of sulphur dissolution in liquid copper ( $0.5S_2(g) = [S]_{Cu}$ ):

$$\ln K_{[S]} = \frac{12300}{T} - 5.4820$$

2. Non-temperature dependence of the activity coefficient of sulphur dissolved in the copper-rich liquid (Liquid I):

$$\ln \gamma_{[S]} = -18.25 \cdot x_{[S]}$$

3. The chemical potential of the sulphur dissolved in copper in infinite dilute solution:

$$\mu_{[S]}^{\infty} = -12404 - 99.643 \cdot T \quad J \cdot (\text{mol}[S])^{-1}$$

4. Non-temperature dependence of the activity of sulphur in Cu-S sulphur-rich liquid (Liquid II) – Fig. 6.

5. Non-temperature dependence of the activity of copper in Cu-S sulphur-rich liquid (Liquid II) – Fig. 7.

6. The equilibrium constant for the reaction of sulphur removal from liquid copper ( $[S]_{Cu} + 2[O]_{Cu} = SO_2(g)$ ):

$$\ln K_{SO_2}^{\infty} = 0.0436 + \frac{17440}{T} + 0.00208 \cdot T$$

*Keywords:* copper, sulphur, thermodynamic properties

### 1. Introduction

Thermodynamic properties of Cu-O, Cu-S and Cu-S-O solutions are vital to understanding of processes of copper metallurgy. This is the second of planned papers concerning these systems. The Cu-S system has a large immiscibility gap as shown schematically in Fig. 1.

Liquid I have limited solubility for sulphur. Thermodynamic properties of solutions containing up to about 1.5 wt.-% sulphur are of great interest for copper fire refining process. Composition of Liquid II ranges from slightly less sulphur than in  $Cu_2S$  to those more than in  $Cu_2S$ . These solutions play important role in the copper-making stage of the copper matte converting operation. For these reasons these liquids were studied quite extensively [1-17].

The thermodynamic properties of Cu-S system were investigated with two different methods. The first method involves equilibration of liquid copper with a gas which generating sulphur in gaseous state ( $S_2(g)$ ) e.g.  $H_2S - H_2$  [1-5,9-10] or  $N_2 - S_2$

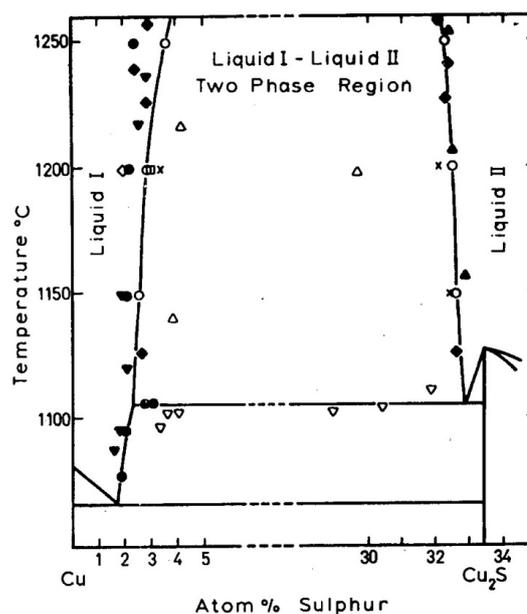
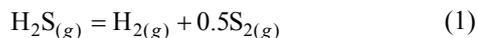


Fig. 1. A portion of the system Cu-S – not to scale-Ref. [10]

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gas mixtures [8]. The generated gaseous sulphur is dissolved in the copper as long as equilibrium between these two phases is attained:



Obtained results with this method do not allow to calculate the equilibrium constant for the reaction (2), because the value of the standard chemical potential of sulphur dissolved in copper ( $\mu_{[\text{S}]}^0$ ) is unknown.

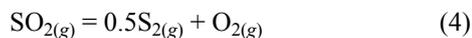
The second method was employed by Taskinen [15], and is based on measurement of electromotive force (emf) of galvanic cell with solid electrolyte conducting oxygen ions ( $\text{O}^{2-}$ ).

The emf of the galvanic cell is related to the oxygen pressure in two half-cells by the relations:

$$-4FE = RT \ln \frac{P_{\text{O}_2}}{P_{\text{O}_2(\text{Ref.})}} \quad (3)$$

where:  $E$  – the electromotive force of the galvanic cell (V),  $F$  – the Faraday constant ( $96487 \text{ J} \cdot \text{V}^{-1}$ ),  $R$  – the universal gas constant ( $8.3143 \text{ J} \cdot \text{K}^{-1}$ ),  $T$  – the temperature (K),  $P_{\text{O}_2}$  – the oxygen partial pressure above the liquid copper (bar),  $P_{\text{O}_2(\text{Ref.})}$  – the oxygen partial pressure in reference electrode (bar).

The partial oxygen pressure ( $P_{\text{O}_2}$ ) above the liquid copper can be determined if the oxygen pressure ( $P_{\text{O}_2(\text{Ref.})}$ ) in the reference electrode is known. A mixture of Ar + 1%  $\text{SO}_2$  was flowing above liquid copper, so gaseous sulphur was generated according to the reaction:



Making use of the equilibrium constant for the reaction (4) and relations (3), the partial pressure of gaseous sulphur can be determined in this half-cell:

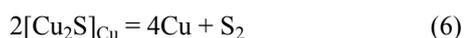
$$P_{\text{S}_2}^{0.5} = K \frac{P_{\text{SO}_2}}{P_{\text{O}_2(\text{Ref.})} \cdot \exp\left(\frac{-4FE}{RT}\right)} \quad (5)$$

$K$  – is the equilibrium constant for the reaction (4).

Also, in this case is impossible to determine the equilibrium constant because of the standard chemical potential of sulphur ( $\mu_{[\text{S}]}^0$ ) is unknown. The objective of this study was to overcome this obstacle and proposed a simple and consistent description of thermodynamic properties of Cu-S solutions.

## 2. Methods reported in the literature for thermodynamic properties description of Cu-S solutions

Sudo [1] arbitrary assumed that the sulphur dissolved in copper exists in the form of  $\text{Cu}_2\text{S}$ , and its decomposition proceeds according to the reaction:



Thanks to this assumption it was possible to calculate the standard Gibbs energy and the equilibrium constant for the reaction (6). However, in the equilibrium constant, the activity of  $\text{Cu}_2\text{S}$  was replaced by sulphur concentration:

$$K = \frac{P_{\text{S}_2}}{[\%S]^2} \quad (7)$$

In addition, he assumed that the copper activity is equal to 1 in solutions Cu- ' $\text{Cu}_2\text{S}$ '. It worth to mention that concentration of  $\text{Cu}_2\text{S}$  is approximately 5 times higher than sulphur concentration in weight percentage.

Schuhmann and Moles [2] utilized the reaction of the sulphur dissolved in liquid copper with hydrogen:



The equilibrium constant for this reaction is given by the relations:

$$K = \frac{P_{\text{H}_2\text{S}}}{a_{[\text{S}]} \cdot P_{\text{H}_2}} \quad (9)$$

Differentiating logarithm of Eq. (9) at constant temperature we can obtain:

$$d(\ln a_{[\text{S}]}) = d\left(\ln \frac{P_{\text{H}_2\text{S}}}{P_{\text{H}_2}}\right) \quad (10)$$

Employing Gibbs-Duhem equation and Eq. (10), one can calculate the activity of copper in Cu-S mixtures:

$$\ln(a_{\text{Cu}}) = \ln(a_{\text{Cu}})_{x_{\text{S}}^B} - \int_{x_{[\text{S}]}^B}^{x_{[\text{S}]}} \frac{x_{[\text{S}]}}{1 - x_{[\text{S}]}} d\left(\ln \frac{P_{\text{H}_2\text{S}}}{P_{\text{H}_2}}\right) \quad (11)$$

where:  $(a_{\text{Cu}})_{x_{\text{S}}^B}$  – the activity of copper in Cu-S solution having sulphur concentration  $x_{[\text{S}]}^B$  mole fraction.

They assumed that the sulphur dissolved in liquid copper exists in  $\text{Cu}_2\text{S}$  form. In addition, they assumed that in solution of  $\text{Cu}_2\text{S}$  composition, the activities of copper as well as  $\text{Cu}_2\text{S}$  are equal to 1. In consequence of these assumptions, the copper activity is higher than 2 for a certain composition.

Hirakiso and co-workers [3] and Yagihashi [4] investigated copper-rich Cu-S solutions and assumed that these solutions behave as ideal ones. The equilibrium constant they expressed by the equation:

$$K = \frac{P_{\text{H}_2\text{S}}}{P_{\text{H}_2} \cdot [\%S]} \quad (12)$$

Alcock [5] concluded that the Henry's law is applicable to copper-rich Cu-S mixtures.

Bale and Toguri [10] determined the activity coefficient of copper for both side of immiscibility region with the relation:

$$\ln \gamma_{\text{Cu}} = \ln \gamma_{\text{Cu}}^B - \int_{x_{[\text{S}]}^B}^{x_{[\text{S}]}} \frac{x_{[\text{S}]}}{1 - x_{[\text{S}]}} d(\ln \gamma_{\text{S}}) \quad (13)$$

They erroneously assumed that the sulphur activity is equal to square roots of sulphur partial pressure ( $a_{\text{S}} = P_{\text{S}_2}^{0.5}$ ). In reality

the activity of sulphur is expressed by the relation  $a_S = K \cdot P_{S_2}^{0.5}$ , where  $K$  is the equilibrium constant of dissolution of sulphur in liquid copper. In the case of diluted Cu-S solution we can assume that  $\gamma_{[Cu]}^B \approx 1$  for  $x_{[S]}^B \rightarrow 0$ . However, in the case of sulphur, the value of  $\gamma_{[S]}^B$  has to be chosen arbitrarily.

Larrain and co-workers [11], Sharma and Chang [12], and Chuang [13] applied an associated solution model for description of the thermodynamic properties of Cu-S mixtures. In all cases they employed the three-suffix Margules equation, with zero ternary interactions. In paper [11] it was assumed that the solution consists of three components: Cu, 'Cu<sub>2</sub>S' and 'CuS'. And in papers [12] and [13] it was postulated that Cu<sub>2</sub>S and 'Cu<sub>2</sub>S' formed Cu-S solutions. These models can describe thermodynamic properties in the composition ranges placed on both sides of immiscibility region.

A disadvantage of this method is that each of these models required 8 adjustable parameters. In such a case the function which is used for determination of these parameters  $Q = \sum_i (q_{i(mod.)} - q_{i(exp.)})^2$  has very shallow minimum, and therefore is very difficult to find the absolute minimum. These adjustable parameters depend very heavily even on a single experimental value ( $q_{i(exp.)}$ ). Hence, a physical meaning of these parameters could be questioned. This thesis can be supported by the fact that authors of paper [12] did not take into consideration Cu-S and S-Cu interactions, which is against to common view that copper and sulphur show considerable chemical affinity.

Niemelä and Taskinen [15] assumed that the activity of sulphur dissolved in liquid copper is equal to square root of the sulphur pressure above the melt. This is the outcome of authors assumption that the standard state of sulphur in liquid copper is the diatomic sulphur gas at 1 bar.

### 3. The Cu-S mixture at infinite dilution as a reference state for sulphur ( $\gamma_{[S]} = 1$ for $x_{[S]} = 0$ )

In the case of infinite diluted Cu-S solution, the equilibrium constant for the reaction (2) can be written by the following relation:

$$K_{[S]} = \frac{x_{[S]} \cdot \gamma_{[S]}}{P_{S_2}^{0.5}} \rightarrow \frac{x_{[S]}}{P_{S_2}^{0.5}} \quad \text{for } x_{[S]} \rightarrow 0 \quad (14)$$

where:  $x_{[S]}$  – the mole fraction of sulphur dissolved in liquid copper,  $\gamma_{[S]}$  – the activity coefficient of the sulphur in liquid copper,  $P_{S_2}$  – sulphur pressure above liquid copper.

In other words, we assume that the activity coefficient of dissolved sulphur in liquid copper at infinite dilution is equal to 1:

$$\gamma_{[S]} = 1 \quad \text{for } x_{[S]} = 0 \quad (15)$$

Figure 2 shows the function  $x_{[S]}/P_{S_2}^{0.5} = f(x_{[S]}, T = \text{const})$ , and limiting value of this function is equal to the equilibrium constant ( $K_{[S]}$ ) at constant temperature.

Utilizing experimental data from several sources [1,3-5,10,15], the equilibrium constants ( $K_{[S]}$ ) for reaction (2) were esti-

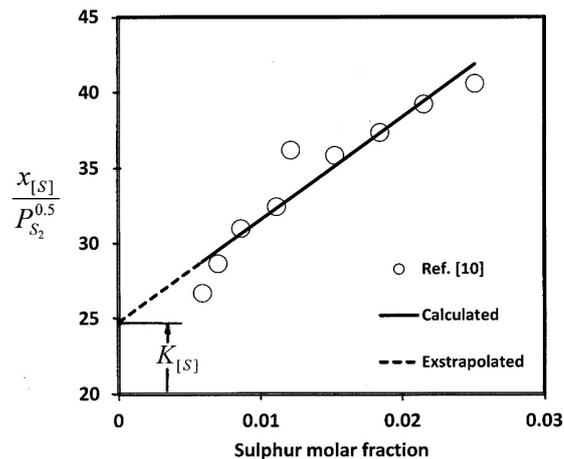


Fig. 2. Variation of  $x_{[S]}/P_{S_2}^{0.5}$  ratio with mole fraction of sulphur dissolved in liquid copper. Points were estimated from data given in paper [10] and obtained at 1423 K. Solid line was calculated with the list square method and dashed line is extrapolation of  $x_{[S]}/P_{S_2}^{0.5}$  ratio to  $x_{[S]} = 0$

ated by extrapolation of a function  $x_{[S]}/P_{S_2}^{0.5} = f(x_{[S]}, T = \text{const})$  to  $x_{[S]} = 0$ . Fig. 2 demonstrates an example of  $K_{[S]}$  estimation. Sulphur pressures ( $P_{S_2}$ ) were estimated for the reaction (1) with thermodynamic data taken from data base of HSC 7 for Windows software. And in the case when data are obtained with emf method, the sulphur pressures were calculated with the Gibbs energy of formation ( $\Delta G_f$ ) for the reaction (4) given in [18] and experimental data reported in paper [15]. Obtained results are plotted in Fig 3.

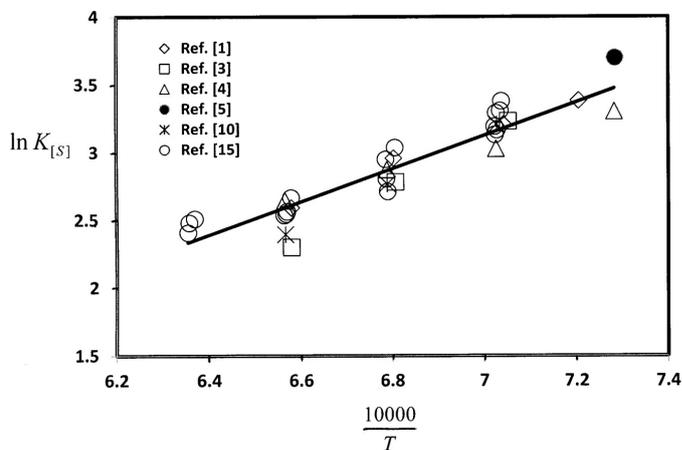


Fig. 3. Dependence of the equilibrium constant of reaction (2) versus temperature. The solid line represents Eq. 16

Making use of the least square method, the straight-line parameters in Fig. 3 were established:

$$\ln K_{[S]} = \frac{12300}{T} - 5.4820 \quad (16)$$

Coupling Eq. (14) and Eq. (16), the following relation can be obtained:

$$\frac{12300}{T} - 5.4820 = \ln \left( \frac{x_{[S]} \cdot \gamma_{[S]}}{P_{S_2}^{0.5}} \right) \quad (17)$$

Rearranging Eq. (17), the activity coefficient of sulphur dissolved in liquid copper can be determined:

$$\ln \gamma_{[S]} = \frac{12300}{T} - 5.4820 - \ln \frac{x_{[S]}}{P_{S_2}^{0.5}} \quad (18)$$

For the computation of  $\ln \gamma_{[S]}$  experimental data reported by Niemelä and Taskinen [15] were employed and the results are illustrated in Fig. 4. A considerable scatter of experimental data does not prevail a temperature dependence of the activity of the sulphur dissolved in liquid copper. In consequence it was assumed that the activity coefficient of sulphur does not depend on temperature. Therefore, the activity of sulphur was described by the relation:

$$\ln \gamma_{[S]} = -18.25 \cdot x_{[S]} \quad (19)$$

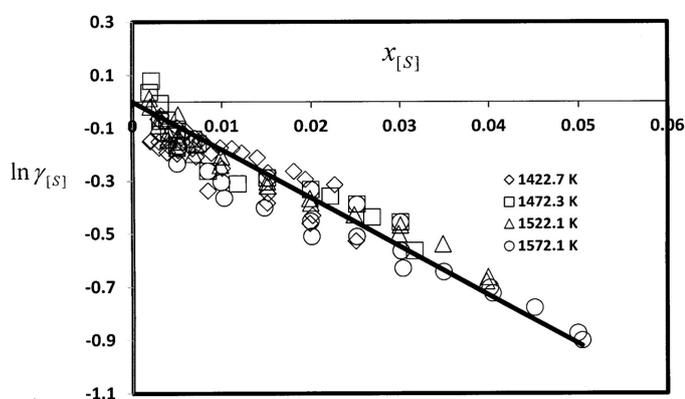


Fig. 4. The relations between activity coefficient of sulphur and its concentration in Cu-S mixture. Points were calculated with experimental data reported in paper [15] and Eq. (18). Solid line represents Eq. (19)

Employing the Gibbs-Duhem equation and relations (19), the activity of copper can be derived:

$$\ln \gamma_{Cu} = 18.25 \cdot (-x_{[S]} - \ln(1 - x_{[S]})) \quad (20)$$

Expanding the term  $\ln(1 - x_{[S]})$  in series, and taking into account two first terms, the activity coefficient of copper can be established:

$$\ln \gamma_{Cu} = 9.125 \cdot x_{[S]}^2 \quad (21)$$

Equation (21) is a very good approximation of the relation (20) for small values of  $x_{[S]}$ , which is the case for copper-rich Cu-S solution (see Fig. 4). For the same reason, the activity coefficient of copper is closed to unity, because of very small value of  $x_{[S]}^2$ .

The Gibbs energy of the reaction of sulphur dissolution in liquid copper is described by the relation:

$$\begin{aligned} \Delta G_{[S]} &= -RT \ln K_{[S]} = \\ &= -102265.8 + 45.578 \cdot T \quad \text{J} \cdot (\text{mol}[S]) \quad (22) \end{aligned}$$

Making use of the Gibbs energy for sulphur dissolution in liquid copper Eq. (22). And in addition, the chemical potential of the sulphur in gaseous state, which was taken from data base of HSC 7 for Windows software. The chemical potential of the

sulphur dissolved in liquid copper at infinity dilute solution is expressed by the relations:

$$\begin{aligned} \mu_{[S]}^\infty &= \Delta G_{[S]} + \frac{1}{2} \mu_{S_{2(g)}}^0 = \\ &= -12404 - 99.643 \cdot T \quad \text{J} \cdot (\text{mol}[S]) \quad (23) \end{aligned}$$

This function ( $\mu_{[S]}^\infty$ ) is very important in thermodynamic examination of copper refining processes (Sulphur removal). The chemical potential of sulphur in liquid copper for any composition can be expressed by the relation:

$$\mu_{[S]} = \mu_{[S]}^\infty + RT \ln a_{[S]} \quad (24)$$

#### 4. Verification of the proposed method for copper-rich Cu-S solution

The activity of copper in copper-rich Cu-S solutions (Liquid I) can be calculated with two independent method.

The first method was to use Eq. (11), written in different but equivalent form:

$$\ln a_{Cu} = \ln a_{Cu}^B - \int_{x_{[S]}^B}^{x_{[S]}} \frac{x_{[S]}}{1 - x_{[S]}} d(\ln P_{S_2}^{0.5}) \quad (25)$$

To calculate the activity of copper with Eq. (25), it was assumed that for the solution with the lowest sulphur concentration ( $x_{[S]}^B$ ), the activity coefficient is closed to 1 ( $\gamma_{[Cu]}^B \approx 1$ ). In addition, the integrand was described by a polynomial of the second order ( $x_{[S]}/(1 - x_{[S]}) = a \cdot (\ln P_{S_2}^{0.5})^2 + b \cdot (\ln P_{S_2}^{0.5}) + c$ ). The values of these polynomial parameters ( $a$ ,  $b$ ,  $c$ ) were estimated with the least square method, and experimental data taken from paper [15].

The second method was to employ Eq. (21), and the activity of copper was calculated with the equation:

$$a_{Cu} = (1 - x_{[S]}) \cdot \exp(9.125 \cdot x_{[S]}^2) \quad (26)$$

Fig. 5 illustrates a very good agreement between these results computed with two independent methods.

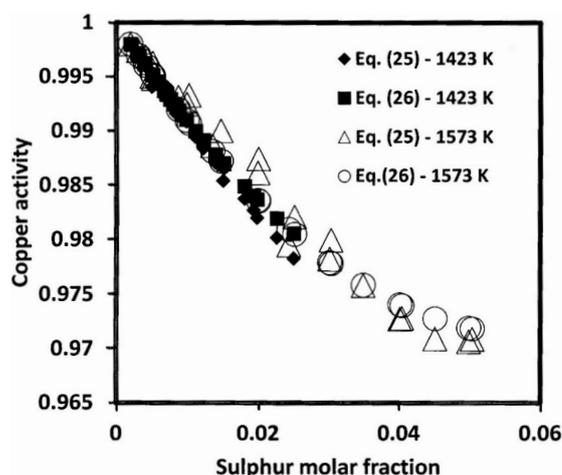


Fig. 5. Comparison between the activities of copper in Cu-S copper-rich mixtures calculated with two independent methods

### 5. Activities of sulphur and copper in sulphur-rich Cu-S melts

The activity coefficient of sulphur in this composition range of Cu-S system was estimated with the equation (18), and the ratio  $x_{[S]}/P_{S_2}^{0.5}$ , which was calculated using the experimental data given in paper [10]. Then the activity of sulphur was calculated, and the results are shown in Fig. 6.

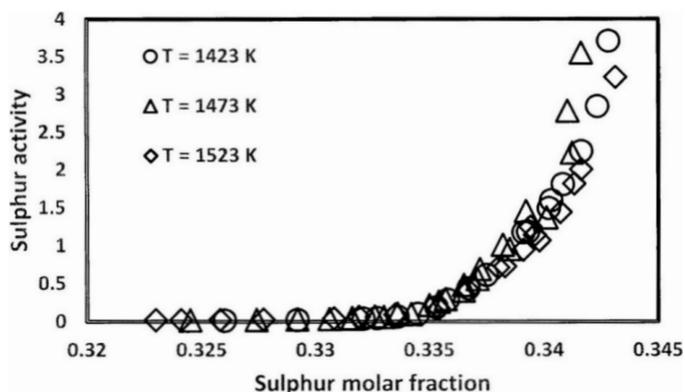


Fig. 6. The activity of sulphur in Cu-S mixture as a function of temperature and composition. The activities were calculated with Eq. (18) and experimental data [10]

The sulphur activities exceed 1, because of the assumption that the activity coefficient of sulphur in infinity dilute solution is equal to unity ( $\gamma_{[S]} = 1$  for  $x_{[S]} = 0$ ). The activity of copper in these mixtures was determined with Eq. (25) and experimental data [10]. The constant of integration ( $\ln a_{Cu}^B$ ) was estimated with the condition of stability of two liquids:

$$a_{Cu}^B = a_{Cu}^{liquid:II}(x_{[S]}, T) = a_{Cu}^{liquid:I}(x_{[S]}, T) \quad (27)$$

where:  $a_{Cu}^{liquid:I}(x_{[S]}, T)$  was calculated with Eq. (26).

Figure 7 demonstrates results of the calculation with experimental data reported in paper [10]. To describe the integrand two spliced polynomials of third order were used ( $x_{[S]}/(1-x_{[S]}) = a \cdot (\ln P_{S_2}^{0.5})^3 + b \cdot (\ln P_{S_2}^{0.5})^2 + c \cdot (\ln P_{S_2}^{0.5}) + d$ ). The coefficients of these polynomials were determined with the least square method.

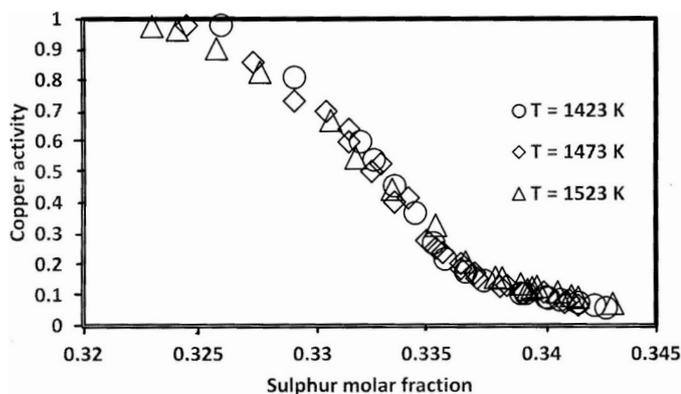


Fig. 7. The activity of copper as a function of temperature and composition of Cu-S mixtures. Calculations were carried out with Eq. (25) and experimental data [10]

In both cases no functions were found which could describe satisfactory the activities of copper and sulphur which varied sharply in a considerably narrow composition range (see Fig. 6 and Fig. 7). Obtained results can be used for examination of the second stage of converting process as well as fire refining process. In copper fire refining process, the final sulphur content should be lower than 20 ppm. To achieve this goal, air is injected into liquid copper:



The dissolved oxygen reacts with the sulphur according to the reaction:



The Gibbs energy change for this reaction can be expressed by the relations:

$$\Delta G_{SO_2}^\infty = \mu_{SO_2(g)}^0 - \mu_{[S]}^\infty - 2 \cdot \mu_{[O]}^\infty \quad (30)$$

where:  $\mu_{SO_2(g)}^0$  – the standard chemical potential of  $SO_2$  in gaseous state,  $\mu_{[S]}^\infty$  – the chemical potential of the sulphur dissolved in liquid copper at infinite dilute solution,  $\mu_{[O]}^\infty$  – the chemical potential of the oxygen dissolved in liquid copper at infinite dilute solution.

Values of  $\mu_{SO_2(g)}^0$  were acquired from the data base of HSC 7 for Windows software. Values of  $\mu_{[S]}^\infty$  were calculated with Eq. (23), and  $\mu_{[O]}^\infty$  with the following relation [19]:

$$\mu_{[O]}^\infty = -57404 - 88.877 \cdot T \quad J \cdot (\text{mol}[O])^{-1} \quad (31)$$

Making use of these data, the Gibbs energy of the reaction of sulphur removal from liquid copper was established:

$$\Delta G_{SO_2}^\infty = -144996 - 0.3629 \cdot T - 0.0173 \cdot T^2 \quad J \cdot (\text{mol}[SO_2])^{-1} \quad (32)$$

The relation (32) is connected with the equilibrium constant for the reaction of sulphur removal from liquid copper:

$$\ln K_{SO_2}^\infty = 0.0436 + \frac{17440}{T} + 0.00208 \cdot T \quad (33)$$

### 6. Conclusion

1. A simple method for description of thermodynamic properties of Cu-S system was put forward in this work. The method is based on the assumption that the activity coefficient of sulphur in liquid copper at infinite dilute solution is equal to unity ( $\gamma_{[S]} = 1$  for  $x_{[S]} = 0$ ). However, for copper, the reference and the standard state is pure copper ( $\gamma_{Cu} = 1$  and  $a_{Cu} = 1$  for  $x_{Cu} = 1$ ).
2. The equilibrium constant for the reaction of sulphur dissolution in liquid copper was established with involvement of the literature data. At 1473 K the equilibrium constant calculated with Eq. (33) is equal to  $3.1 \cdot 10^6$ .

3. The equilibrium constant enables to estimate the activity coefficient of sulphur in mixtures on both sides of immiscibility region.
4. The activity coefficient of sulphur in copper-rich solutions do not show temperature dependence. A similar behaviour was observed for the oxygen in Cu-O solutions [19]. It is very likely, that the activity coefficient of the sulphur is a slow function of temperature, and experimental errors blurred this dependence.
5. The activity of copper in copper-rich mixtures (Liquid I) does not differ considerably from unity. However, for sulphur-rich solutions (Liquid II), the activity of copper decreases very sharply within a very narrow composition range about Cu<sub>2</sub>S.
6. The activity of sulphur decreases with sulphur content increase for copper-rich solutions (Liquid I), however for sulphur-rich mixtures a very steep variation of sulphur activity is observed, and it exceeds considerably unity.
7. If neglected sulphur-oxygen interaction in Cu-S-O mixtures, then the equilibrium pressure of SO<sub>2</sub> can be estimated with use of equations [19], [33] and the activity coefficient of oxygen in Cu-O mixture [19]:

$$\ln \gamma_{[O]} = -8.382 \cdot x_{[O]}$$

Assuming that at the end of the fire refining process of copper, oxygen concentration is equal to 0.6 wt.-%, and sulphur concentration 20 ppm, for these conditions estimated SO<sub>2</sub> pressure is very small ( $P_{SO_2} < 1$  bar).

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