

## SOLUTION THERMODYNAMICS AN COPPER-OXYGEN SYSTEM

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### **Abstract**

*This work presents the study of some thermodynamic properties of the Cu-O system, which represent the base of several technological processes in the pyrometallurgy of copper. The research have been determined several thermodynamic measurements activity and activity coefficient of oxygen in liquid copper-oxygen function on the temperature and oxygen concentration influence on them. The experimental results have been compared to various thermodynamic models reference to metallurgical melting for alloys and discovery of some structural information on the melting in the studied system.*

*Keywords: copper, activity, activity coefficient, atomic ratio, oxygen, interaction coefficient*

### **1. INTRODUCTION**

The copper-oxygen system presents a challenging task for thermodynamic modelling. Extensive measurement of the thermodynamic properties of the liquid phase between the Cu and Cu<sub>2</sub>O composition using e.m.f. were made by Taskinen [1] in good agreement with each other, Kulkarni [2] made measurements in a rather limited temperature interval (1513 to 1623 K), where as Taskinen [1] covered a considerably larger temperature interval (1373 to 1723 K). Osterwald [3] made measurement in the oxygen-rich liquid and of the Cu<sub>2</sub>O -liquid and Cu<sub>2</sub>O liquid equilibrium. The value suggested by Sigworth and Elliot [7] is in a good agreement with the present result.

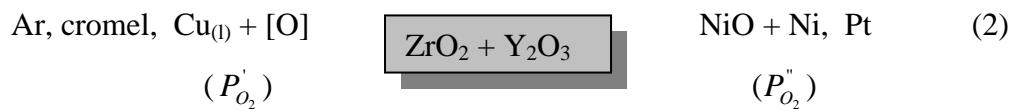
In contrast to the rather limited number of measurement at high oxygen content, a large number of thermodynamic investigations of the Cu-rich liquid have been made using electromotive force.

The binary intends to determine the activity and oxygen activity coefficient for different concentrations as a temperature function around 1150-1300°C.

Based on the dependence between the activity coefficient and the atomic ratio the activity limit coefficient for solutions at infinite dilution has been determined and with its help it was established the equation of the free standard enthalpy as a function of the reaction temperature:



The experiments were realised using an electrochemical method based on the electromotive force of equilibrium measurements for a typical galvanic cell:



The difference between oxygen potential of the Cu<sub>(l)</sub> + [O] solution and NiO-Ni mechanic mixture determines an electric potential difference between the two cell electrodes (E). Thermodynamically the cell equilibrium is in perfect agreement with the chemical equilibrium of reaction:



## 2. EXPERIMENTAL RESULTS

The research on the Cu-O system have been done at temperatures between 1150 and 1300°C. Based on the electromotive force measurements, the activity and activity coefficients as a function of the atomic ratio and temperature have been calculated.

Experimental data for activity and activity coefficients, determination as a function of the electromotive force, given by [9]:

$$\ln \gamma_o = 23211 \frac{E}{T} + \frac{121140}{T} + 2,7793 \ln T - 65,2667 \quad (4)$$

$$\text{and } \gamma = \frac{a_o}{X_o} \quad (5)$$

where: E - represents the cell electromotive force;  
 $a_o$  - copper 's oxygen activity;  
 $\gamma_o$  - oxygen activity coefficient;  
T - temperature;  
 $X_o$  - oxygen atomic ratio.

The graphic representation of the activity coefficient logarithm as a function of the oxygen atomic ratio at constant temperature (figure 1-4) emphasises a parabolic variation, which suggests a typical equation [4]:

$$\ln \gamma_o = \ln \gamma_o^0 + \varepsilon_o^0 X_o + \rho_o^0 X_o^2 \quad (6)$$

where:  $\gamma_o^0$  - represent the activity limit coefficient;  
 $\varepsilon_o^0$  - first order interaction thermodynamic parameter;  
 $\rho_o^0$  - second order interaction thermodynamic parameter.

For the oxygen limit activity coefficient and first interaction thermodynamic parameter determination, a typical parabolic has been considered:  $y = a + bx + cx^2$

where:  $y = \ln \gamma_o$ ;  $x = X_o$  (atomic ratio).

From these notation, we obtain  $b = \ln \gamma_o^0$ ,  $a = \varepsilon_o^0$  and  $c = \rho_o^0$ .

To establish the analytical equations, the least-squares optimisation was used [5].

After finishing the calculus, the following equation which shown the variation of the activity coefficient as a function of the oxygen atomic ratio for:

$$T = 1523 \text{ K}$$

$$\ln \gamma_o = -1,8635 - 9,135 X_o + 285,357 X_o^2 \quad (7)$$

$$T = 1573 \text{ K}$$

$$\ln \gamma_o = -1,640 - 8,607 X_o + 276,700 X_o^2 \quad (8)$$

T=1523 K

$$\ln \gamma_o = -1,4312 - 8,113 X_o + 254,100 X_o^2 \quad (9)$$

T=1573 K

$$\ln \gamma_o = -1,2375 - 7,651 X_o + 246,435 X_o^2 \quad (10)$$

Relation (7-10) were obtained by using medium values determined for each experiment and are graphically represented in figures (1-4).

From the expressions of the variation equation of the activity coefficient logarithm, activity coefficient values first and second order interaction thermodynamic parameters values were obtained and they are given in table 1.

*Table 1* Activity coefficient logarithm, first and second order interaction thermodynamic parameters value of oxygen in liquid copper

Nr. crt.	T (K)	$x = \frac{1}{T} \cdot 10^4, K^{-1}$	$y = \ln \gamma_o^0$	$\gamma_o^0$	$z = \varepsilon_o^0$	$\rho_o^0$
1	1423	7,0274	-1,8635	0,1551	-9,135	285,357
2	1473	6,7889	-1,640	0,1939	-8,607	276,700
3	1523	6,5660	-1,4312	0,2390	-8,113	254,100
4	1573	6,3573	-1,2375	0,2901	-7,651	246,435

For determination of analytical equation of these functions, the least-squares optimisation method was used, on the base of the following equations were obtained:

$$\gamma_o^0 = -\frac{9539}{T} + 4,83 \quad (11)$$

$$\varepsilon_o^0 = -\frac{22135}{T} + 6,42 \quad (12)$$

$$\rho_o^0 = \frac{623724}{T} - 151,3 \quad (13)$$

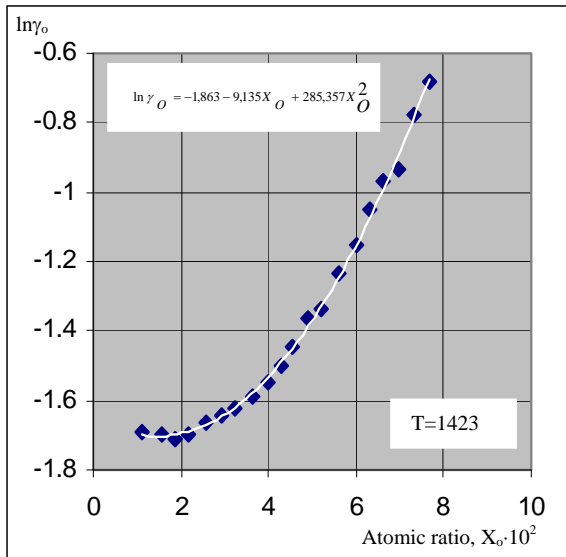


Figure 1 Logarithmic activity coefficient of oxygen at infinite dilution in liquid copper at T=1423K.

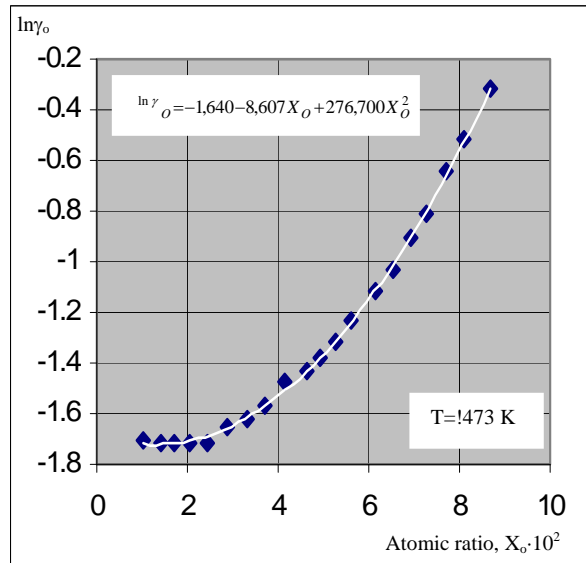


Figure 2 Logarithmic activity coefficient of oxygen at infinite dilution in liquid copper at T=1473K.

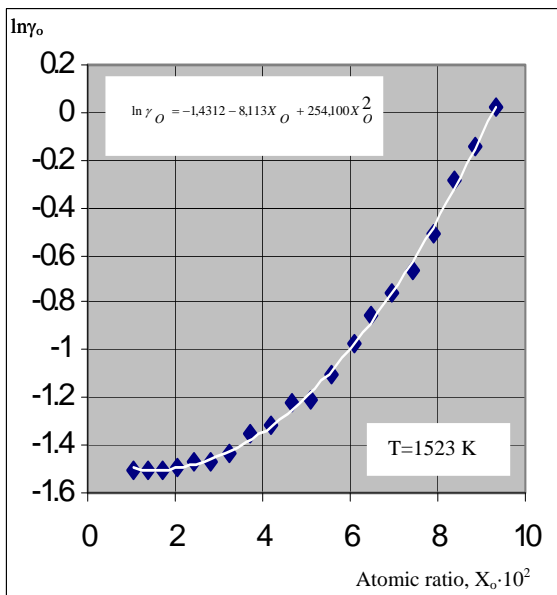


Figure3 Logarithmic activity coefficient of oxygen at infinite dilution in liquid copper at T=1523K.

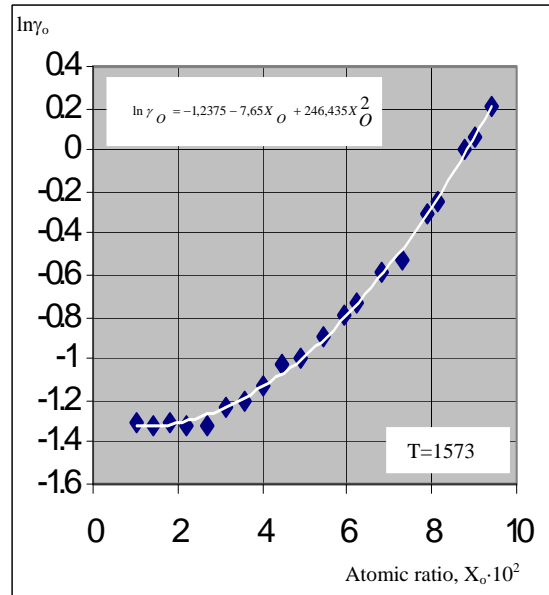


Figure 4 Logarithmic activity coefficient of oxygen at infinite dilution in liquid copper at T=1573K.

### 3. DISCUSSION

The second parameters is defined in general [4] by:  $\rho_k^i = \lim_{P,T} \left( \frac{\partial^2 \ln \gamma_k}{\partial x_i} \right)$ . Runs was

a chosen for the analysis due to its large oxygen concentration range, and the parameters are calculated at 1150-1300°C by using the method of least squares. The results are shown in fig.5.

Scatter in the numerical values is relatively large (about  $\pm 30\%$ ), but the magnitude of the second order parameter is significant, its contribution to the activity coefficient of oxygen being considerable in the conditions of copper fire-refining.

The equations, which express the dependence of the activity, limit coefficient as a function of the atomic ratio established in the present work (7-10) allowed the determination of the activity limit coefficient and the thermodynamic interaction parameters.

The values of the activity limit coefficient presented in table 1 are in a very good agreement with the values obtained by Kulkarni [2] and who indicated the following values: 0,245 at 1250°C and 0,285 at 1300°C.

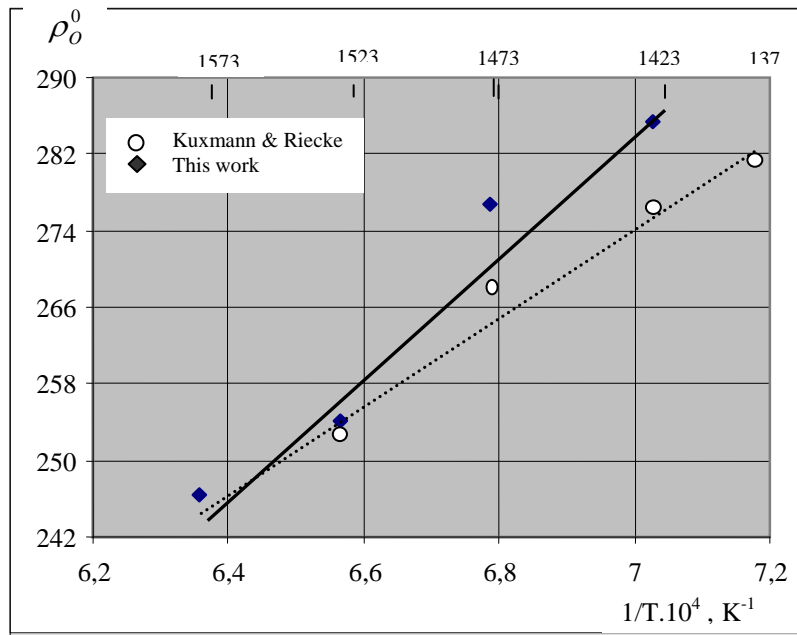
Taskinen [1] used an electrochemical method with a reference electrode from air and established the following values for the activity coefficient: 0,258 at 1250°C and 0,315 at 1300°C which are in very good agreement with the values presented in table 1.

Regarding the first order interaction coefficient of oxygen in liquid copper-oxygen, the present work show an increase of this one from -7,651 to -8,11 once the temperature grows from 1250 to 1300°C and second order parameters an increase of this one from 254,1 to 246,43 from 1250 to 1300°C.

Jacob and Jeffes [6] have established the following dependence of the first order coefficient of oxygen in liquid copper-oxygen:  $\varepsilon_o^0 = 7,83 - \frac{23950}{T}$ . The equation established in the present work (12) is in a good agreement with Jacob and Jeffes.

Figure 5 show a comparison of the present results with the work of Kuxmann and Riecke [8] regarding the second order parameters. Scatter in the numerical values is relatively large but the magnitude of the second order parameter is significant and is also in fair agreement with the assessment of Kuxmann and Riecke.

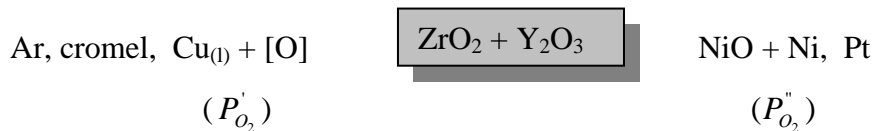
Thus, the obtained values in the present work for the first and second order interaction coefficient of oxygen are a bit smaller if experimental errors are considered which can get to 30% or even more, and become significantly close.



**Fig. 5** Second order oxygen interaction coefficient in liquid copper-oxygen alloys.

#### 4. CONCLUSIONS

Liquid equilibrium and solution thermodynamics of oxygen in liquid copper-oxygen alloys have been studied by using a solid state oxygen concentration cell with lime stabilized zirconium as the solid electrolyte. The experimental cell can be written schematically as



Liquid surface were measured at a temperature interval of 1150-1300<sup>0</sup>C. The activity coefficient of oxygen at infinite dilution in liquid copper is:  $\gamma_o^0 = -\frac{9539}{T} + 4,83$  and its deviation from the Henrian behaviour, i.e. the first and second order interaction coefficient of oxygen, is:  $\varepsilon_o^0 = -\frac{22135}{T} + 6,42$ ;  $\rho_o^0 = \frac{623724}{T} - 151,3$ .

The graphic representation of the activity coefficient logarithm as a function of the oxygen atomic ratio at constant temperature emphasises a parabolic variation, which suggests a typical equation:  $\ln \gamma_o = \ln \gamma_o^0 + \varepsilon_o^0 X_o + \rho_o^0 X_o^2$

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chosen for the analysis due to its large oxygen concentration range, and the parameters are calculated at 1150-1300°C by using the method of least squares.

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