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# Equilibrium fugacities of the $Cu_2O$-CuO and Cu-$Cu_2O$ buffers

by *Tjerk Peters**

## Abstract

The oxygen fugacity-temperature relationships of the $Cu_2O/CuO$ and $Cu/Cu_2O$ buffers were measured with a solid electrolyte cell ($ZrO_2$ with $Y_2O_5$). For the $Cu_2O/CuO$ buffer the equation $\log fO_2 = 8.76 - \frac{12653}{Tabs}$ and for the $Cu/Cu_2O$ buffer $\log fO_2 = 7.35 - \frac{17760}{Tabs}$ were obtained. These new equations lie within the spead of equations given in the literature.

## Introduction

For the experimental determination of mineral equilibria of systems where components of different oxidation states participate, solid buffers have come to use. In the fundamental work of EUGSTER (1957) and EUGSTER and WONES (1962) on the stability relations of ironbearing minerals, the nickel-nickel-oxyde, iron-wüstite, wüstite-magnetite, magnetite-hematite, fayalite-quarz-magnetite buffers were used. Since then several additional buffers like cobalt-cobaltoxide (CHOU 1978), graphite-methane (EUGSTER and SKIPPEN 1967), manganese oxyde buffers (HUEBNER and SATO 1970) have been applied in hydrothermal experiments. For low oxygen-fugacities there are quite a number of buffers that can be applied. The range of higher oxygenfugacities, however, is not so well-covered. Of late the $Cu_2O$-CuO has come into use (ABS-WURMBACH et al. 1980), (ABS-WURMBACH et al. 1983) for systems of high oxidation state. For the equilibrium fugacities of this buffer the experimental determinations of MAH et al. (1967) can be used or they can be calculated from the thermodynamic data in the tables of ROBIE and WALDBAUM (1968) or ROBIE, HEMINGWAY and FISCHER (1978). These fugacities differ about 0,6 log $fO_2$ unit. Furthermore, in routine experimental work commercially available pure chemicals are used and not specially synthesized from ultra-specpure metals. For these reasons the fugacity-temperature relationships of the copperoxide buffers

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were determined with a solid electrolyte cell. Kiukkola and Wagner (1957) already used a solid electrolyte to measure the equilibriumfugacity of the Ni-NiO-buffer.

## Experimental

### *Starting materials*

| | |
|---|---|
| CuO | Copper (II) oxide powder, "pro analyse" from Merck, Darmstadt, FRG, were used. The amount of impurities like Fe and Pb should be less than 0.05%. |
| $Cu_2O$ | Copper (I) oxide powder, pure from Merck, Darmstadt, FRG, which is not in the catalogue was used. The amount of the metal-oxyde impurities should be less than 0.1%. |
| Cu | Copper fine powder, "pro analyse" from Merck, Darmstadt, FRG, was used. The amount of impurities of other metals is less than 0.01%. |

### *Equipment*

The equipment used for this study is very similar to the one described by Sato (1972). It has a double cell arrangement to be able to minimize the oxygen transfer across the yttria (10%) stabilized zirconia tubes and not to deplete the buffering capacity of the samples. To obtain the same oxygen fugacity as the $Cu$-$Cu_2O$ and $Cu_2O$-$CuO$ buffers mixtures of $N_2$ + 1% $H_2$ with $N_2$ + 2% $CO_2$ and $N_2$ + 2 $CO_2$ with air were used respectively. Samples were hold in quartz—or zirconia crucibles and capped by Pt—Foils. In the three-zoned furnace the sample, electrodes and Pt/Rh-thermoelement were in the centre of the hot zone, that showed a temperature variation of less than 1 ° over a length of 5 cm. The samples were heated or cooled in steps of 50 °C and held at these temperatures till the emf changed less than 0,2 mV over a period of one hour. Numerous heating and cooling cycles were performed, resulting in a large number of reversals. Air was used as reference gas.

### *Calibration*

Between runs the equipment was calibrated with nickel-nickeloxide. During these calibrations it was found that NiO had to be recrystallized for at least 3 days at 1050 °C. After this treatment our results were within 0,01 log $fO_2$-unit of the data given by Huebner (1971), who used the same kind of equipment, and by Schwab and Küstner (1981).

## Results

### *$Cu_2O$-CuO*

Oxygen fugacity measurements of this buffer are represented in figure I, the symbols indicating the side towards equilibrium was attained. The data show a linear relationship between log $fO_2$ and 1/T abs. The experimental results from Mah et al. (1967) lie at somewhat higher oxygen fugacities, like the values from the thermochemical data of Robie and Waldbaum (1968). The thermochemical data of Robie, Hemingway and Fischer (1978), however, fall at lower oxygen fugacities.

The equation resulting from 80 data points is:

$$\log fO_2 = 8.76 - \frac{12653}{T_{abs}}$$

The standard deviation for log $fO_2$ = 0,02. The equation is for the temperature range 700–1050 °C.

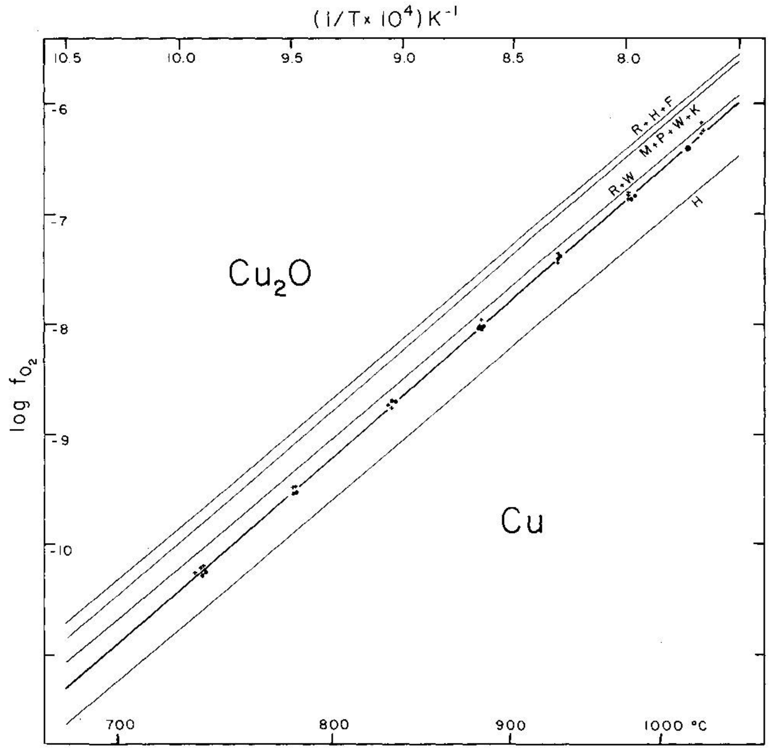

*Fig. 1:* Equilibrium $Cu_2O$-CuO. Dots indicate equilibrium points with decreasing temperature and crosses with increasing temperature. Also shown are experimental curve by Mah et al (1967) M + P + W + K and curves based on thermochemical data by Robie and Waldbaum (1968), (R + W), and by Robie et al. (1978) R + H + W.

### *$Cu$-$Cu_2O$*

The data obtained for this buffer result in an equilibrium curve that lies halfway (fig. 2) between the curve obtained from the equation given by HUEBNER (1971) and the data from MAH et al. (1967). For the range 700-1050 ° the equation is:

$\log fO_2 = 7.35 - \frac{17760}{T_{abs}}$ (standard deviation for $\log fO_2 = 0.02$)

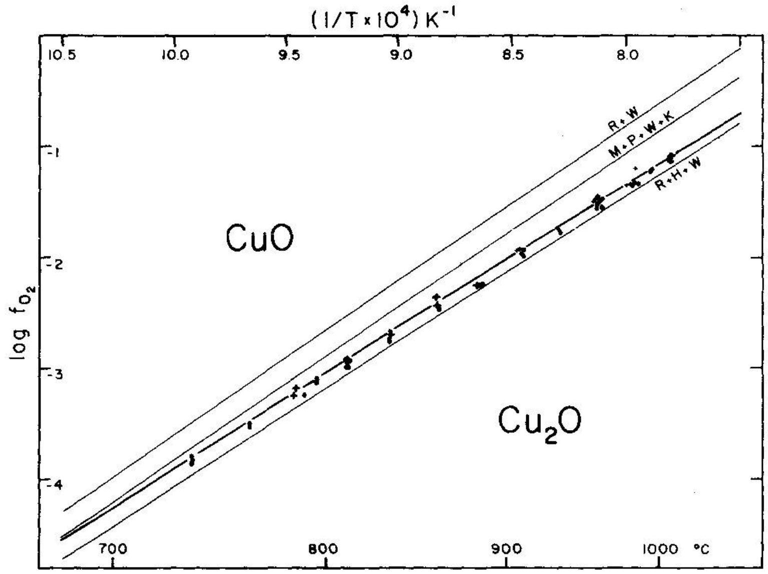

*Fig. 2:* Equilibrium Cu-$Cu_2O$. Abbreviations as in fig. I. H = curve based on equation given by HUEBNER (1971).

## Discussion

With the new data it should be possible to use the $Cu_2O$-CuO buffer in hydrothermal experiments when high oxygen fugacities are needed.

An unexpected result of this investigation was the appreciable influence of the cristallinity of the nickeloxyde on the resulting $fO_2$ of the Ni-NiO buffer. Especially in short runs (< 3 days) this factor might lower the oxygen fugacity of 0.5-0.8 log $fO_2$ units. A similar effect was observed by KÜSTNER (1979), who attributed it however to impurities of Si, Al and Mn.

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