

Zeitschrift: Schweizerische mineralogische und petrographische Mitteilungen =
Bulletin suisse de minéralogie et pétrographie

Band: 63 (1983)

Heft: 1

Artikel: Equilibrium fugacities of the Cu₂O-CuO and Cu-Cu₂O buffers

Autor: Peters, Tjerk

DOI: <https://doi.org/10.5169/seals-48720>

Nutzungsbedingungen

Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften auf E-Periodica. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. Das Veröffentlichen von Bildern in Print- und Online-Publikationen sowie auf Social Media-Kanälen oder Webseiten ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. [Mehr erfahren](#)

Conditions d'utilisation

L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. La reproduction d'images dans des publications imprimées ou en ligne ainsi que sur des canaux de médias sociaux ou des sites web n'est autorisée qu'avec l'accord préalable des détenteurs des droits. [En savoir plus](#)

Terms of use

The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. Publishing images in print and online publications, as well as on social media channels or websites, is only permitted with the prior consent of the rights holders. [Find out more](#)

Download PDF: 18.02.2026

ETH-Bibliothek Zürich, E-Periodica, <https://www.e-periodica.ch>

Equilibrium fugacities of the Cu₂O-CuO and Cu-Cu₂O buffers

by *Tjerk Peters**

Abstract

The oxygen fugacity-temperature relationships of the Cu₂O/CuO and Cu/Cu₂O buffers were measured with a solid electrolyte cell (ZrO₂ with Y₂O₅). For the Cu₂O/CuO buffer the equation $\log fO_2 = 8.76 - \frac{12653}{T_{abs}}$ and for the Cu/Cu₂O buffer $\log fO_2 = 7.35 - \frac{17760}{T_{abs}}$ were obtained. These new equations lie within the spread 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 SKIPPER 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 Cu₂O-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 fO₂ 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

* Min.-petr. Institut der Universität Bern, Baltzer-Strasse 1, CH-3012 Bern.

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%.

Cu₂O 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-Cu₂O and Cu₂O-CuO buffers mixtures of N₂ + 1% H₂ with N₂ + 2% CO₂ and N₂ + 2 CO₂ with air were used respectively. Samples were held 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 fO₂-unit of the data given by HUEBNER (1971), who used the same kind of equipment, and by SCHWAB and KÜSTNER (1981).

Results

Cu₂O-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 $\log f_{O_2}$ and $1/T \text{ abs}$. 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:

$$\log f_{O_2} = 8.76 - \frac{12653}{T_{\text{abs}}}$$

The standard deviation for $\log f_{O_2} = 0.02$. The equation is for the temperature range 700-1050 °C.

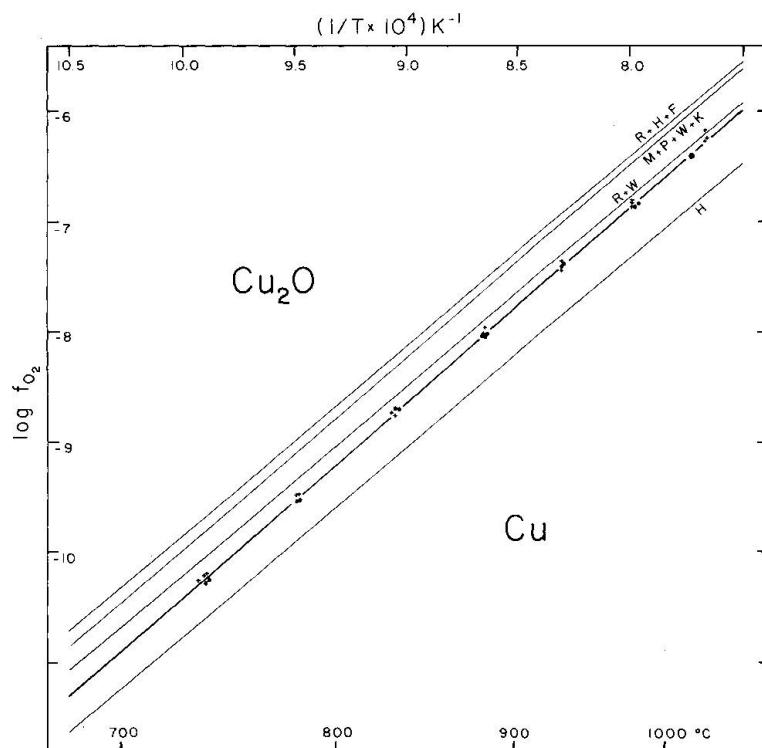


Fig. 1: Equilibrium Cu₂O-CuO. Dots indicate equilibrium points with decreasing temperature and crosses with increasing temperature. Also shown are experimental curve by MAH et al (1967) M + P + W + K and curves based on thermochemical data by ROBIE and WALDBAUM (1968), (R + W), and by ROBIE et al. (1978) R + H + W.

Cu-Cu₂O

The data obtained for this buffer result in an equilibrium curve that lies half-way (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:

$$\log f_{O_2} = 7.35 - \frac{17760}{T_{\text{abs}}} \quad (\text{standard deviation for } \log f_{O_2} = 0.02)$$

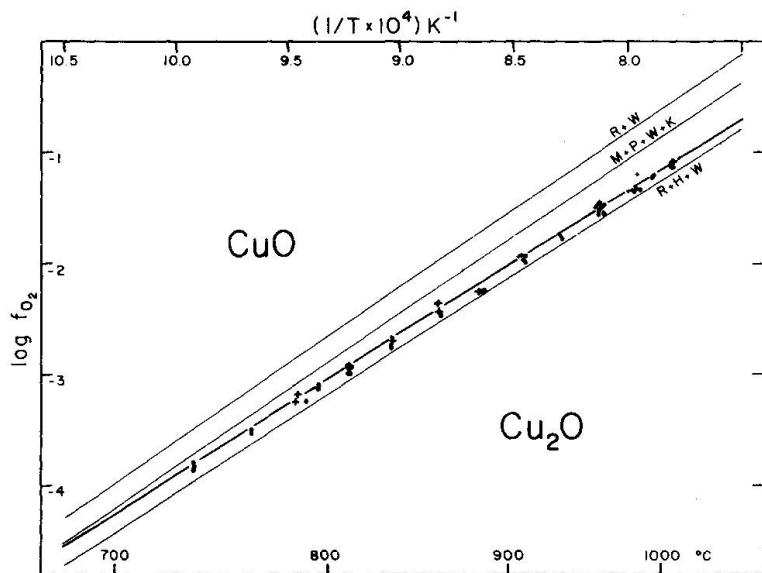


Fig. 2: Equilibrium Cu-Cu₂O. Abbreviations as in fig. I.
H = curve based on equation given by HUEBNER (1971).

Discussion

With the new data it should be possible to use the Cu₂O-CuO buffer in hydrothermal experiments when high oxygen fugacities are needed.

An unexpected result of this investigation was the appreciable influence of the crystallinity of the nickel oxyde on the resulting fO₂ of the Ni-NiO buffer. Especially in short runs (< 3 days) this factor might lower the oxygen fugacity of 0.5-0.8 log fO₂ units. A similar effect was observed by KÜSTNER (1979), who attributed it however to impurities of Si, Al and Mn.

Acknowledgements:

Prof. Dr. R. G. Schwab (Erlangen) is thanked for the stimulating review of this paper, Dr. M. Sato (Reston, Va) for his hospitality in his laboratory, A. Liechti (Bern) for the construction and upkeep of the equipment.

References:

ABS-WURMBACH, I., LANGER, K. and SCHREYER, W. (1980): Studies on braunite stability relations in the system Mn-Si-O at controlled oxygen fugacity, XII, General Meeting IMA, Orléans 1980, Collected Abstr. 8147.

ABS-WURMBACH, I., PETERS, T.J., LANGER K. and SCHREYER, W. (1983): Phase relations in the system Mn-Si-O: an experimental and petrological study. N. Jhb. Min. 146, 258-279.

CHOU, I. M. (1978): Calibration of oxygen buffers at elevated P and T using the hydrogen fugacity sensor. Am. Min. 63, 690-703.

EUGSTER, H. P. (1957): Heterogenous reactions involving oxidation and reduction at high pressures and temperatures. J. Chem. Phys. 26, 1760-1761.

EUGSTER, H. P. and WONES, D. R. (1962): Stability relations of the ferruginous biotite, annite. J. Petrol. 3, 82-125.

EUGSTER, H. P. and SKIPPER, G. (1967) Igneous and metamorphic reactions involving gas equilibria. In: Researches in Geochemistry 2, Ed. P. H. Abelson. Wiley, New York, 377-396.

HUEBNER, J.S. (1971): Buffering techniques for hydrostatic systems at elevated pressures. Research techniques for high pressure and high temperature. Ed. G.C. Ulmer, Springer, New York, 1971, pp. 123-177.

HUEBNER, J.S. and SATO, M. (1970): The oxygen fugacity-temperature relationships of manganese oxide and nickel oxide buffers. Am. Min. 55, 934-952.

KIUKKOLA, K. and WAGNER, G. (1957): Measurements on galvanic cells involving solid electrolytes. J. Electrochem. Soc. 104, 379-387.

KÜSTNER, D. (1979): Elektrochemische Bestimmung von Redoxgleichgewichten und thermodynamischen Daten im System Mg-Fe-Si-O. Dissertation Univ. Erlangen-Nürnberg.

MAH, A. D., PANKRATZ, L. B., KELLER, W. W. and KING, E. G. (1967): Thermodynamic data for cuprous and cupric oxydes. U.S. Bur. Mines Report. Inv. 7026, 20 p.

ROBIE, R. A. and WALDBAUM, D. A. (1968): Thermodynamic properties of Minerals and related Substances at 298.15° K and One Atmospheric Pressure and at Higher Temperatures. Geol. Survey Bull. 1259, 256 p.

ROBIE, R. A., HEMINGWAY, B. S. and FISCHER, J. R. (1978): Thermodynamic Properties of Minerals and related Substances at 298.15 K and 1 Bar Pressure and at Higher Temperature. Geol. Survey Bull. 1452, 456 p.

SATO, M. (1972): Intrinsic oxygen fugacities of iron-bearing oxide and silicate minerals under low total pressure. Geol. Soc. Am. Mem. 135, p. 289-307.

SCHWAB, R. G. and KÜSTNER, D. (1981): Die Gleichgewichtsfugazitäten technologisch und petrologisch wichtiger Sauerstoffpuffer. N. Jhb. Miner. Abh. 140-2, 111-142.

Manuscript received 10 March, 1983.