Phase Relations and Thermodynamic Properties of Condensed Phases in the System Ca-Cu-O

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The isothermal sections of the phase diagram for the system Ca-Cu-O at 1073 and 1223 K have been determined. Several compositions in the ternary system were quenched after equilibration, and the phases present were identified by optical microscopy, X-ray diffraction, and electron probe microanalysis. Two ternary compounds Ca_2CuO_3 and $Ca_{0.828}CuO_{1.93}$ were identified at 1073 K. However, only Ca_2CuO_3 was found to be stable at 1223 K. The thermodynamic properties of the two ternary compounds were determined using solid-state cells incorporating either an oxide or a fluoride solid electrolyte. The results for both types of cells were internally consistent. The compound $Ca_{0.828}CuO_{1.93}$, which can also be represented as $Ca_{15}Cu_{18}O_{35}$, has been identified in an earlier investigation as $Ca_{0.828}CuO_2$. Using a novel variation of the galvanic cell technique, in which the emf of a cell incorporating a fluoride electrolyte is measured as a function of the oxygen potential of the gas phase in equilibrium with the condensed phase electrodes, it has been confirmed that the compound $Ca_{0.828}CuO_{1.93}$ ($Ca_{15}Cu_{18}O_{35}$) does not have significant oxygen nonstoichiometry. Phase relations have been deduced from the thermodynamic data as a function of the partial pressure of oxygen for the system Ca-Cu-O at 873, 1073, and 1223 K.

Introduction

Because of the discovery of superconducting compounds in the systems Ca-Sr-Bi-Cu-O and Ca-Ba-Tl-Cu-O,[1,2] there is considerable interest in phase relations in these systems. A prerequisite for understanding phase equilibria in the five-component systems is an adequate definition of phase relations in the bounding binary and ternary subsystems. As part of a larger program of research on ternary systems containing copper,[3-6] this paper reports determinations of phase diagrams and thermodynamic properties of condensed phases in the system Ca-Cu-O.

Phase relations in the system CaO-CuO-Cu_2O as a function of temperature and oxygen partial pressure (10^4–10^5 Pa) were first studied by Gadalla and White[7] using a thermobalance. They reported only one stable ternary compound, Ca_2CuO_3, in the system. The structure of the compound is orthorhombic, with space group *Immm*.[8] Another phase, $CaCu_2O_3$, was reported by Teske and Muller-Buschbaum[9] and was said to be stable only above 1223 K by Brewer and Eysel.[10] The structure of this compound is orthorhombic, with space group *Pmmm*.[9,10] Roth et al.[11] have studied phase relations in the system CaO-CuO-O_2. They have identified three ternary phases: Ca_2CuO_3, $CaCuO_2$, and $CaCu_2O_3$. The compound $CaCu_2O_3$ was reported to be stable between 1258 and 1293 K. A revised phase diagram of the system CaO-CuO-O_2 published by Roth et al.[12] indicates a stability range from 1258 to 1291 K for $CaCu_2O_3$ in air. The compound $CaCuO_2$ was found to have the composition $Ca_{0.828}CuO_2$.[12] A structural investigation of the compound $Ca_{0.828}CuO_2$ by X-ray diffraction from single crystals has been reported by Siegrist et al.[13] The structure of the compound is pseudoorthorhombic and the symmetry is close to that of space group *Fmmm*. The crystal structure is related to the $NaCuO_2$ type. The exact oxygen content of this compound has not been measured. It can perhaps be better characterized as $Ca_{0.828}CuO_{2-x}$. The literature does not contain a complete report on phase relations in the entire system Ca-Cu-O. Hence phase relations have been systematically investigated at 1073 and 1223 K. Samples containing various mixtures of oxides were equilibrated in pure oxygen and in evacuated quartz ampules. Samples containing metallic phases were equilibrated in evacuated cells made of iron. After equilibration the samples were quenched in liquid nitrogen and their phase composition was determined using X-ray diffraction, supplemented in a few cases by electron probe microanalysis (EPMA). The exact oxygen content of the compound $Ca_{0.828}CuO_{2-x}$ was determined by the hydrogen reduction method.

Thermodynamic properties of ternary oxides in the system Ca-Cu-O have not been determined yet. Therefore, solid-state galvanic cells were designed to measure the standard Gibbs' free energy of formation of ternary oxides, based on the study of phase relations in the system. Extensive thermodynamic measurements using three

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[1] Maeda, A. H.; Tanaka, Y.; Fukutomi, N.; Asano, T. *Jpn. J. Appl. Phys.* **1988**, *27*, L209.

[2] Sheng, Z. Z.; Hermann, A. M. *Nature* **1988**, *332*, 55-58, 138.

[3] Jacob, K. T.; Mathews, T. *J. Mater. Chem.* **1991**, *1*, 545.

[4] Jacob, K. T.; Mathews, T. *J. Am. Ceram. Soc.* **1992**, *75*, 3225.

[5] Jacob, K. T.; Mathews, T.; Hajra, J. P. *Met. Trans.*, in press.

[6] Mathews, T.; Jacob, K. T. *J. Am. Ceram. Soc.*, in press.

[7] Gadalla, A. M. M.; White, J. *Trans. Brit. Ceram. Soc.* **1966**, *65*, 181.

[8] Teske, C. L.; Muller-Buschbaum, H. *Z. Anorg. Allg. Chem.* **1970**, *379*, 234.

[9] Teske, C. L.; Muller-Buschbaum, H. *Z. Anorg. Allg. Chem.* **1969**, *370*, 134.

[10] Brewer, K. H.; Eysel, W. Powder Diffraction File Card No. 34-284, 1982, JCPDS.

[11] Roth, R. S.; Rawn, C. J.; Ritter, J. J.; Burton, B. P. *J. Am. Ceram. Soc.* **1989**, *72*, 1545.

[12] Roth, R. S.; Hwang, N. M.; Rawn, C. J.; Burton, B. P.; Ritter, J. J. *J. Am. Ceram. Soc.* **1991**, *74*, 2148.

[13] Siegrist, T.; Roth, R. S.; Rawn, C. J.; Ritter, J. J. *Chem. Mater.* **1990**, *2*, 192.

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galvanic cells with CaF_2 as the solid electrolyte and two cells with $(Y_2O_3)ZrO_2$ as the solid electrolyte have been performed. The Gibbs' free energy of formation of each cuprate can be derived from measurements with either solid electrolyte. Studies using the two solid electrolytes provide a cross check on the measured thermodynamic data. Solid-state cells provide the most accurate method now available for the measurement of the Gibbs' free energy of oxide ceramics, especially at moderate temperatures.[14]

A novel technique, described elsewhere,[4] has been used to find the excess oxygen content of the cuprates. From the variation of the emf of a cell, incorporating CaF_2 solid electrolyte, as a function of oxygen chemical potential of the gas phase in equilibrium with the solid electrodes containing the cuprate under investigation, the oxygen excess or deficiency of the compound has been evaluated. This technique supplements information on nonstoichiometry obtained from chemical analysis.

Experimental Techniques

1. Materials. The starting materials used for the preparation of interoxide compounds were powders of CuO and $CaCO_3$, each of purity greater than 99.99%. $CaCO_3$ contained in a calcia crucible was decomposed at 1073 K under vacuum to give CaO. The CaO thus obtained was found to be very reactive. The compound Ca_2CuO_3 was prepared by heating a mixture of CaO and CuO in the molar ratio 2:1 at 1240 K for ~30 h in prepurified oxygen atmosphere followed by quenching in liquid nitrogen. The oxides CaO and CuO were weighed and mixed, either dry or with acetone, using an agate mortar and pestle. The handling of CaO was done in a drybox to minimize its reaction with moisture and oxides of carbon and sulfur. The compound $Ca_{0.828}CuO_{2-x}$ was prepared with a CaO to CuO molar ratio of 45.3:45.7, by heating a mixture at 1073 K in ambient oxygen for ~100 h. The pellets were ground and reprocessed thrice during this period. The formation of ternary oxides were confirmed by X-ray diffraction. The Cu, Ca, and Cu_2O used in the study were of 99.9% purity. Single crystals of CaF_2 and polycrystalline tubes of yttria-stabilized zirconia, used as solid electrolytes, and calcia crucibles were obtained from commercial sources. The gases oxygen and argon were of purity greater than 99.999%. They were dried by passing through columns of silica gel, anhydrous $Mg(ClO_4)_2$ and P_2O_5. Mixtures of argon and oxygen were prepared by mixing metered streams of each gas in a tower filled with glass beads. The flow rates of the gases were controlled by mass flow controllers.

2. Determination of Phase Diagram. The phase relations in the ternary system Ca–Cu–O were explored by equilibrating different mixtures of elements and compounds at 1073 and 1223 K, followed by quenching in liquid nitrogen and phase identification. The equilibration period was ~30 h at 1073 K and ~22 h at 1223 K. Preliminary experiments indicated that these holding times were sufficient to attain equilibrium. Several pellets made from mixtures of CaO and CuO, contained in zirconia or calcia crucibles, were equilibrated in pure, dry, flowing oxygen at a pressure of 1.01×10^5 Pa using an apparatus similar to that described elsewhere.[3] Each sample pellet was placed on a small presintered sacrificial pellet of its own composition. The mass of each sample was determined before and after equilibration. A small mass increase was observed during equilibration of mixtures for which the ratio $(n_{Cu}/n_{Ca} + n_{Cu}) > 0.33$, where n_i is the molar amount of component i. This indicates that the compound $Ca_{0.828}CuO_{2-x}$ contains excess oxygen with respect to component oxides CaO and CuO. Samples containing Cu or Cu_2O were equilibrated in evacuated quartz ampules to prevent oxidation. Samples containing Ca–Cu alloys were equilibrated in ampules made of iron and sealed under argon at 10^4 Pa. The samples were quenched, ground, and repelletized twice during the period of equilibration. The phases present in the equilibrated samples were identified by optical microscopy, X-ray diffraction and in a few cases by electron probe microanalysis (EPMA). The compositions of the equilibrated samples are shown in Figures 1 and 2.

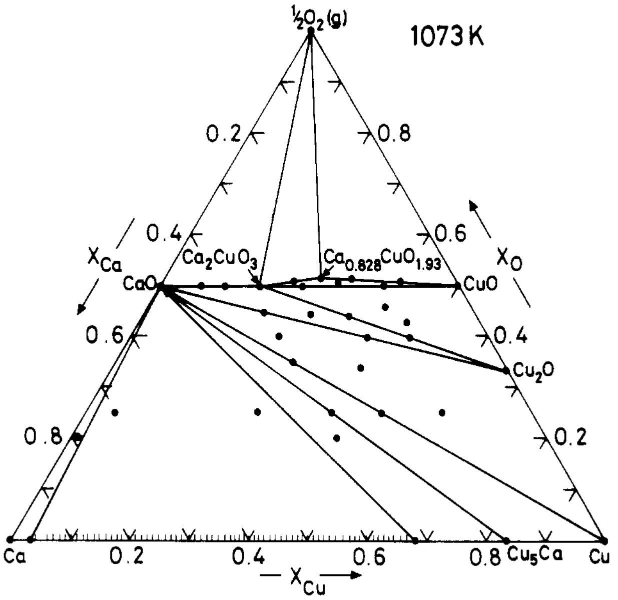

Figure 1. Isothermal section of the ternary phase diagram for the system Ca–Cu–O at 1073 K.

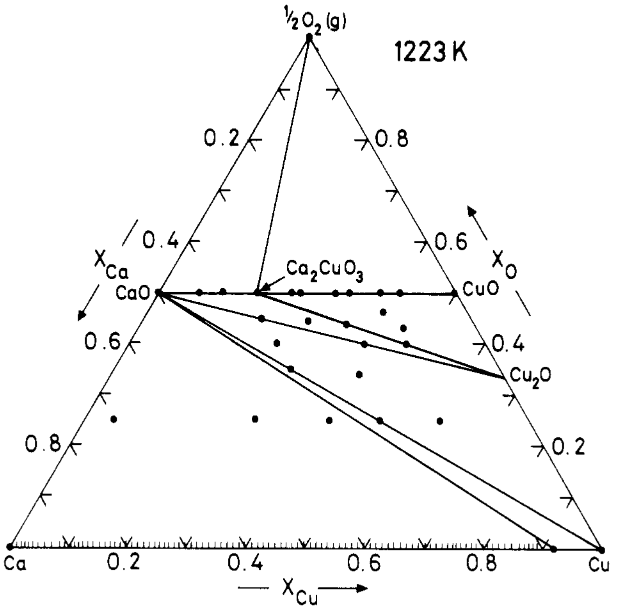

Figure 2. Phase diagram for the system Ca–Cu–O at 1223 K.

The oxygen content of $Ca_{0.828}CuO_{2-x}$ was determined by hydrogen reduction at 1223 K. The hydrogen reduction produced CaO and Cu. From the mass change during reduction determined using a microbalance, the oxygen content of $Ca_{0.828}CuO_{2-x}$ was evaluated. The $Ca_{0.828}CuO_{2-x}$ samples for oxygen analysis was prepared by two different procedures. In the first method, the sample was equilibrated in flowing oxygen at 1073 K for ~30 h and then quenched in liquid nitrogen. In the second method, a pellet of $Ca_{0.828}CuO_{2-x}$ was equilibrated via the gas phase with a three-phase mixture containing $Ca_{0.828}CuO_{2-x}$, Ca_2CuO_3, and CuO in an evacuated quartz ampule shown in Figure 3. Only oxygen was exchanged between the single-phase $Ca_{0.828}CuO_{2-x}$ and the three-phase mixture, since it has appreciable partial pressure. It is assumed that the other elements were not present in the gas. The ampule was quenched after equilibration for ~30 h and the oxygen content of $Ca_{0.828}CuO_{2-x}$ was determined by analysis.

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[14] Pratt, J. N. *Met. Trans.* **1990**, *21A*, 1223.

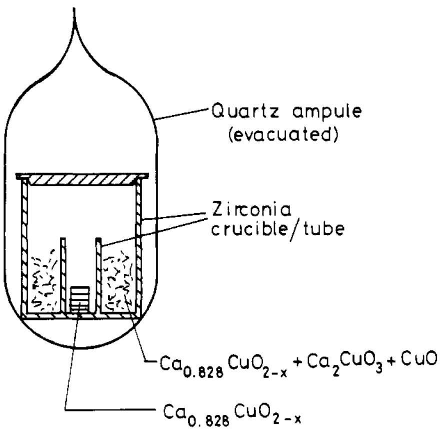

Figure 3. Evacuated quartz capsule for equilibration of single phase $Ca_{0.828}CuO_{2-x}$ with the three-phase mixtures CuO + Ca_2CuO_3 + $Ca_{0.828}CuO_{2-x}$.

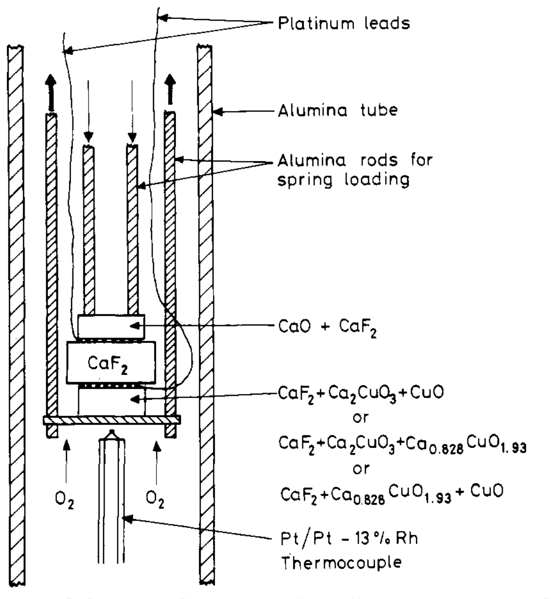

Figure 4. Schematic diagram of the cell arrangement used for emf measurements using CaF_2 solid electrolyte.

3. Emf Measurements Using CaF_2 Electrolyte. The activity of CaO in the different phase fields of the system Ca–Cu–O and the Gibbs' energy of formation of ternary oxides were measured using galvanic cells incorporating CaF_2 as the solid electrolyte, operated under pure oxygen at a pressure of 1.01×10^5 Pa. The emf of the following cells were measured as a function of temperature:

$$\text{Pt, } O_2\text{, CaO} + CaF_2|CaF_2|CaF_2 + Ca_2CuO_3 + \text{CuO, } O_2\text{, Pt} \quad \text{(I)}$$

$$\text{Pt, } O_2\text{, CaO} + CaF_2|CaF_2|CaF_2 + Ca_2CuO_3 + Ca_{0.828}CuO_{1.93}, O_2\text{,Pt} \quad \text{(II)}$$

$$\text{Pt, } O_2\text{, CaO} + CaF_2|CaF_2|CaF_2 + Ca_{0.828}CuO_{1.93} + \text{CuO, } O_2\text{, Pt} \quad \text{(III)}$$

The cells are written such that the right-hand electrodes are positive. A single crystal of CaF_2 was used as the solid electrolyte. The reference electrode consisted of pure CaO. Addition of CaF_2 to the oxide electrodes was necessary to obtain reproducible results. A stacked-pellet assembly shown in Figure 4 was used for emf measurements on cells I to III. Since the equilibrium fluorine pressure over each electrode is extremely low, there is no danger of transport of fluorine from one electrode to the another via the gas phase.

The cell assembly was housed inside a vertical resistance furnace such that electrodes were maintained in the constant temperature zone. A foil of stainless steel, wrapped over the outer alumina tube surrounding the cell, was grounded to minimize induced emf on the platinum leads. The cell temperature was measured by a Pt/Pt–13% Rh thermocouple placed adjacent to the measuring electrode. The temperature of the cell was controlled within ±1 K.

The time required to attain constant emf varied from 3 to 27 h depending on the temperature of measurement, longer periods being required at lower temperatures. The reversibility of the emf was checked by microcoulometric titration in both directions. By the passage of a small direct current (~50 μA for 4 min) through the cell, the fluorine chemical potential at each electrode was altered by an essentially infinitesimal amount. After the passage of current the emf of the cell was monitored as a function of time. Reversibility of the cell was established when the emf returned to the same value after forward and reverse titrations at the same temperature. The reproducibility of the emf was also verified by making measurements during several cycles of increasing and decreasing temperature. Emf was also monitored as a function of the flow rate of the gas in the range 2–4 mL s^{-1}. To check for possible temperature gradient across the cell, the emf of a symmetric cell, with CaO + CaF_2 electrodes on both sides of the CaF_2 electrolyte, was measured as a function of temperature. The emf was in the range ±0.2 mV. X-ray diffraction analysis of the electrodes after each experiment confirmed that there was no change in their phase composition during the emf measurement.

The emf of cells I–III at 973 K were also measured as a function of partial pressure of oxygen in the gas phase over the electrodes. Pure oxygen at controlled pressures and flowing O_2 + Ar mixtures were used to set the chemical potential of oxygen over the electrodes.

4. Emf Measurement Using $(Y_2O_3)ZrO_2$ Electrolyte. The oxygen potential corresponding to the two three-phase mixtures in the system Ca–Cu–O was measured using galvanic cells based on $(Y_2O_3)ZrO_2$ as a function of temperature. The cells studied can be represented as

$$\text{Pt,}Cu_2O + Ca_2CuO_3 + \text{CaO}|(Y_2O_3)ZrO_2|\text{CuO} + Cu_2O\text{, Pt} \quad \text{(IV)}$$

$$\text{Pt,CuO} + Ca_2CuO_3 + Ca_{0.828}CuO_{2-x}|(Y_2O_3)ZrO_2|O_2(1.01 \times 10^5\text{Pa}),\text{Pt} \quad \text{(V)}$$

No attempt was made to measure the low oxygen potentials established by the equilibrium between Ca–Cu alloys and CaO. The solid electrolyte is expected to exhibit significant electronic conduction under such conditions. The solid electrolyte was taken in the form of a long tube closed at one end, so that the gas phase over each electrode was physically separated from the other. The apparatus used was similar to that described by Kale and Jacob.[15] A schematic diagram of the apparatus for measurements on cell V is shown in Figure 5. The three-phase electrode was prepared by ramming a mixture of phases against the closed end of an alumina tube, with a platinum lead embedded in the mixture. The CuO + $Ca_{0.828}CuO_{2-x}$ + Ca_2CuO_3 was in the molar ratio 1:2:1. The reference electrode for cell V was pure oxygen flowing at 3 mL s^{-1} through the inside of the zirconia electrolyte tube. The end of the zirconia tube in contact with oxygen was platinized. A platinum wire was spring loaded against the platinized surface using an alumina gas inlet tube. The apparatus was designed to reduce the volume of the free space above the electrodes.

In the case of cell IV the reference electrode was prepared by ramming a mixture of Cu_2O and CuO in 1:2 molar ratio inside the zirconia tube, with a platinum lead embedded in the mixture. The phase mixture Cu_2O + Ca_2CuO_3 + CaO was taken in the molar ratio 1:2:1. Each electrode compartment was initially flushed with argon gas. The argon flow was then cut off and the electrodes were allowed to establish their equilibrium oxygen partial pressures. When the equilibrium oxygen pressure becomes appreciable, a flowing stream of argon was found to carry away a significant amount of oxygen.

The reversibility and reproducibility of the emf were established by procedures similar to those used for cells based on CaF_2. The phase composition of the electrodes after each emf run was checked by X-ray diffraction.

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(15) Kale, G. M.; Jacob, K. T. *Chem. Mater.* **1989**, *1*, 515.

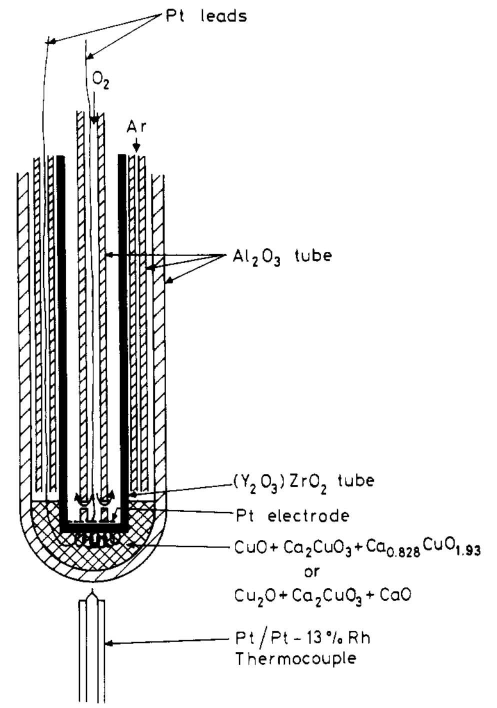

Figure 5. Schematic diagram of cell V based on $(Y_2O_3)ZrO_2$ solid electrolyte.

Results and Discussion

1. Phase Diagram. The isothermal sections of the equilibrium phase diagram of the system Ca–Cu–O at 1073 and 1223 K, obtained from phase analysis of equilibrated samples, are shown in Figures 1 and 2, respectively. The phase relations were found to be independent of the starting compounds used for the preparation of a sample with a specific overall composition. Two ternary oxide phases Ca_2CuO_3 and $Ca_{0.828}CuO_{2-x}$ are stable at 1073 K, but only Ca_2CuO_3 is stable at 1223 K. The compound $Ca_{0.828}CuO_{2-x}$ coexists with CuO, Ca_2CuO_3, and O_2 at 1073 K. It contains oxygen in excess of a mixture of CaO and CuO or Ca_2CuO_3 and CuO. The ratio of Ca to Cu in $Ca_{0.828}CuO_{2-x}$ was confirmed by EPMA. There are no ternary oxide phases in the pseudobinary section CaO–Cu_2O, with copper in monovalent state. This is in contrast to the behavior of SrO–Cu_2O and BaO–Cu_2O pseudobinaries, where compounds of the type MCu_2O_2 (M = Sr, Ba) are stable.[4,16] Solid Cu, intermetallic compound Cu_5Ca, liquid Ca–Cu alloys, and solid Ca are in equilibrium with CaO. The oxygen content of $Ca_{0.828}CuO_{2-x}$ at 1073 K in equilibrium with pure oxygen was found to be 1.93 (±0.01). The oxygen content of this phase in equilibrium with CuO and Ca_2CuO_3 at 1073 K was 1.92 (±0.01). Since the difference is within the experimental uncertainty, the composition of the phase can be written as $Ca_{0.828}CuO_{1.93}$. This contrasts with the formula $Ca_{0.828}CuO_2$ given by Roth et al.[12] The empirical formula for the phase is $Ca_{15}Cu_{18}O_{35}$. The deficiency of Ca in the compound is partly compensated by oxygen deficiency and partly by electron hole localization on either Cu^{2+} or O^{2-} ions. There is no corresponding phase in the Sr–Cu–O and Ba–Cu–O systems. However, in the Sr–Cu–O system there is a phase with the formula $Sr_{14}Cu_{24}O_{41}$, which contains oxygen in excess of a mechanical mixture of SrO and CuO.[4]

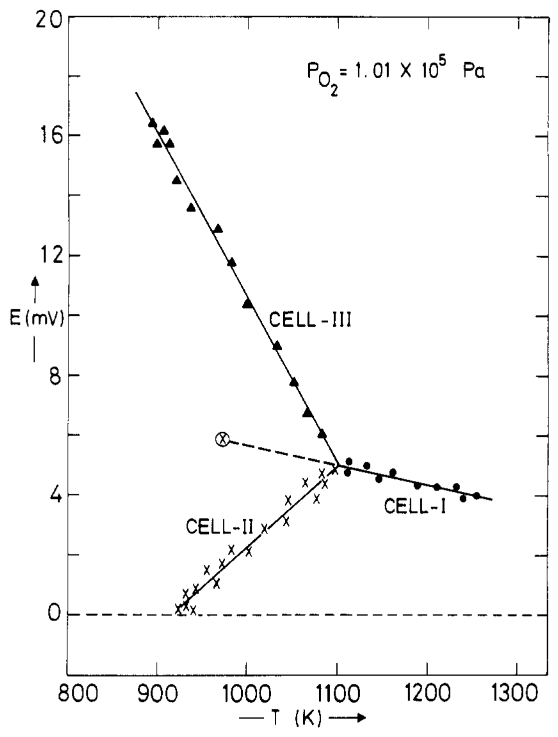

Figure 6. Variation of emfs of cells I–III, based on CaF_2 solid electrolyte, with temperature.

2. Galvanic Cells with CaF_2 Electrolyte. The variation of the reversible emf of cells (I–III) based on CaF_2 as the solid electrolyte with temperature is shown in Figure 6. The cells were operated in pure oxygen at a pressure of 1.01×10^5 Pa. Within the experimental error the emf is a linear function of temperature for each cell. The emf of cells I and III decreases with temperature, whereas the emf of cell II increases with temperature. The emf of all three cells converge at a temperature of 1102 (±1) K to a value of 5 mV. The emf of cells II and III was stable only below 1100 K, whereas that of cell I was stable only in the interval $1105 < T < 1260$ K. This reflects the instability of the phase $Ca_{0.828}CuO_{1.93}$ at $T > 1102$ K in pure O_2. The decomposition temperature of $Ca_{0.828}CuO_{1.93}$ is expected to decrease with the partial pressure of oxygen in the ambient atmosphere. Therefore, the "triple point" should move to low temperature if the oxygen partial pressure is reduced. The electrochemical reactions at the electrodes of cells I–III are listed in Table I. Since oxygen partial pressure over each electrode is the same, the activity of CaO at each electrode is inversely proportional to the fluorine partial pressure. The activity of CaO is defined by the phases present at each electrode. The least-squares regression equation for emf, the overall cell reaction and the corresponding change in the Gibbs' energy for each cell are summarized in Table II. The error limits correspond to twice the standard deviation. Since the compound $Ca_{0.828}CuO_{1.93}$ contains excess oxygen, the reactions corresponding to cells II and III contain gaseous oxygen either as a reactant or product. From the emf of cells I to III, the standard Gibbs' energy of formation of the two ternary compounds can be derived. The values are given in Table III. Auxiliary thermodynamic data are not required to compute Gibbs' energy of formation of ternary oxides from CaO, CuO, and O_2.

It is interesting to note that the emf of cell II becomes zero at 920 K. This suggests that Ca_2CuO_3 is unstable relative to CaO and $Ca_{0.828}CuO_{1.93}$ at $T < 920$ K in pure

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(16) Jacob, K. T.; Mathews, T.; Hajra, J. P. *Mater. Sci. Eng.* **1992**, *15*, 63.

Table I. Electrochemical Reactions at Electrodes of Cells I–III

cell	reaction at the right electrode	reaction at the left electrode
I	$CuO(s) + 2CaF_2(s) + O_2(g) + 4e^- \rightarrow Ca_2CuO_3(s) + 4F^-$	$2CaO(s) + 4F^- \rightarrow 2CaF_2(s) + O_2(g) + 4e^-$
II	$Ca_{0.828}CuO_{1.93}(s) + 1.172CaF_2(s) + 0.535O_2(g) + 2.344e^- \rightarrow Ca_2CuO_3(s) + 2.344F^-$	$1.172CaO(s) + 2.344F^- \rightarrow 1.172CaF_2(s) + 0.535O_2(g) + 2.344e^-$
III	$CuO(s) + 0.828CaF_2(s) + 0.465O_2(g) + 1.656e^- \rightarrow Ca_{0.828}CuO_{1.93}(s) + 1.656F^-$	$0.828CaO(s) + 1.656F^- \rightarrow 0.828CaF_2(s) + 0.414O_2(g) + 1.656e^-$

Table II. Measured Emf's of Solid-State Cells and the Gibbs' Energy Changes for the Corresponding Cell Reactions

cell	temp range, K	cell reaction	emf, mV	$\Delta G°$, J/mol
I	1110–1260	$2CaO(s) + CuO(s) \rightarrow Ca_2CuO_3(s)$	$12.4 - 6.71 \times 10^{-3}T$ (±0.2)	$-4790 + 2.59T$ (±80)
II	925–1100	$Ca_{0.828}CuO_{1.93}(s) + 1.172CaO(s) \rightarrow Ca_2CuO_3 + 0.51O_2(g)$	$-25.1 + 2.73 \times 10^{-2}T$ (±0.4)	$5680 - 6.17T$ (±90)
III	900–1100	$0.828CaO(s) + CuO(s) + 0.051O_2(g) \rightarrow Ca_{0.828}CuO_{1.93}(s)$	$65.5 - 5.49 \times 10^{-2}T$ (±0.3)	$-10\,470 + 8.77T$ (±50)
IV	925–1250	$4CaO(s) + 2CuO(s) \rightarrow 2Ca_2CuO_3(s)$	$51.1 - 2.81 \times 10^{-2}T$ (±0.7)	$-9860 + 5.42T$ (±135)
V	925–1100	$1.4155CuO(s) + Ca_2CuO_3(s) + 0.1232O_2(g) \rightarrow 2.4155Ca_{0.828}CuO_{1.93}(s)$	$437 - 0.396T$ (±1)	$-20\,780 + 18.8T$ (±50)

Table III. Comparison of the Gibbs' Energies of Formation of Ternary Phases in the System Ca–Cu–O Obtained from Galvanic Cells Incorporating Fluoride and Oxide Electrolytes

		$\Delta G°$, J mol^{-1}	
phase	formation reaction	CaF_2 electrolyte	$(Y_2O_3)ZrO_2$ electrolyte
Ca_2CuO_3	$2CaO(s) + CuO(s) \rightarrow Ca_2CuO_3(s)$	$-4790 + 2.59T$ (±80)	$-4930 + 2.71T$ (±70)
$Ca_{0.828}CuO_{1.93}$	$0.828CaO(s) + CuO(s) + 0.051O_2(g) \rightarrow Ca_{0.828}CuO_{1.93}(s)$	$-10\,470 + 8.77T$ (±50)	$-10\,640 + 8.92T$ (±90)

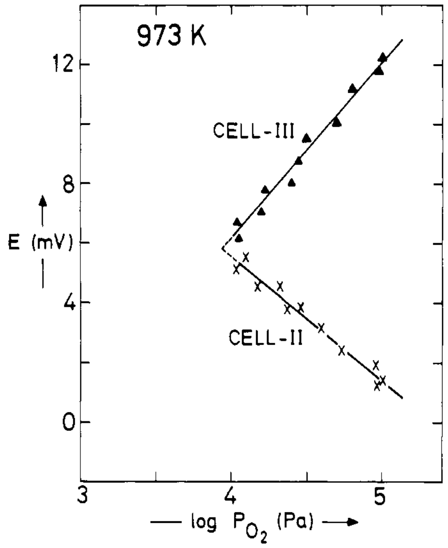

Figure 7. Dependence of the emf of cells II and III on partial pressure of oxygen in the gas phase over the electrodes at 973 K.

O_2. So far there have been no other hints in the literature about the possible metastability of Ca_2CuO_3 at low temperature. At lower partial pressures of oxygen, the temperature range for the stability of Ca_2CuO_3 is enlarged. It may be difficult to verify the predicted instability of Ca_2CuO_3 directly because of the slow rate of diffusion at the low temperatures.

Since the reactions corresponding to cells II and III involve oxygen gas, their emfs are predicted to vary with the partial pressure of oxygen. The experimental verification of this dependence at 973 K is shown in Figure 7. The emf of cell II decreases with partial pressure of oyxgen, whereas that of cell III increases with increase in oxygen partial pressure. As the partial pressure of oxygen is reduced, the emf of cells II and III approach each other and finally become equal at $P_{O_2} = 8.7 \times 10^3$ Pa. Below this partial pressure of oxygen, the compound $Ca_{0.828}CuO_{1.93}$ is not stable at 973 K. The emf and temperature corresponding to the equality of emf of cells II and III under reduced oxygen partial pressure is plotted on Figure 6. The point lies on the extension to low temperature of the line representing the emf of cell I. This provides an additional check of the internal consistency of the emf data. The dependence of emf on log P_{O_2} is approximately linear for both cells. This suggests that the stoichiometry of $Ca_{0.828}CuO_{1.93}$ does not change significantly with the partial pressure of oxygen. On the basis of the overall reaction corresponding to cells II and III given in Table II, it can be readily shown that

$$\partial E_{II}/\partial \log P_{O_2} = -0.051 \times 2.303RT/\eta_{II}F = -4.2 \text{ mV} \quad (1)$$

$$\partial E_{III}/\partial \log P_{O_2} = 0.051 \times 2.303RT/\eta_{III}F = 5.94 \text{ mV} \quad (2)$$

where F is the faraday constant and $\eta_{II} = 2.344$ and $\eta_{III} = 1.656$ are the number of electrons involved in the electrochemical reactions corresponding to cells II and III, respectively. The lines drawn in Figure 7 correspond to the theoretical slope. The lines represent the data adequately, confirming that 0.051 mol of O_2 gas are involved in the cell reactions and that the oxygen nonstoichiometric parameter x in $Ca_{0.}38_{28}CuO_{2-x}$ is 0.07. This supports the analytical determination of oxygen content. Thus, from a study of the dependence of the emf of cells, with a fluoride electrolyte and oxide electrodes, as a function of the partial pressure of oxygen in the ambient atmosphere, information on the nonstoichiometry of the oxide present at the electrode can be obtained.

3. Galvanic Cells with $(Y_2O_3)ZrO_2$ Electrolyte. The oxygen potentials corresponding to two three-phase fields in the system Ca–Cu–O have been measured using cells IV and V. The variation of the reversible emf of the cells with temperature is shown in Figure 8. A mixture of Cu_2O and CuO is used as the reference electrode in cell IV. For cell V pure flowing oxygen at a pressure of 1.01×10^5 Pa is used as the reference electrode. The equations for emf obtained from regression analysis, the cell reactions, and the corresponding Gibbs' energy changes are summarized in Table II. The oxygen potential corresponding to the three-phase mixtures can be represented by the equations

$$\Delta\mu_{O_2}(Cu_2O + Ca_2CuO_3 + CaO) = -280\,610 + 198.7T\ (\pm 500)\ \text{J mol}^{-1} \quad (3)$$

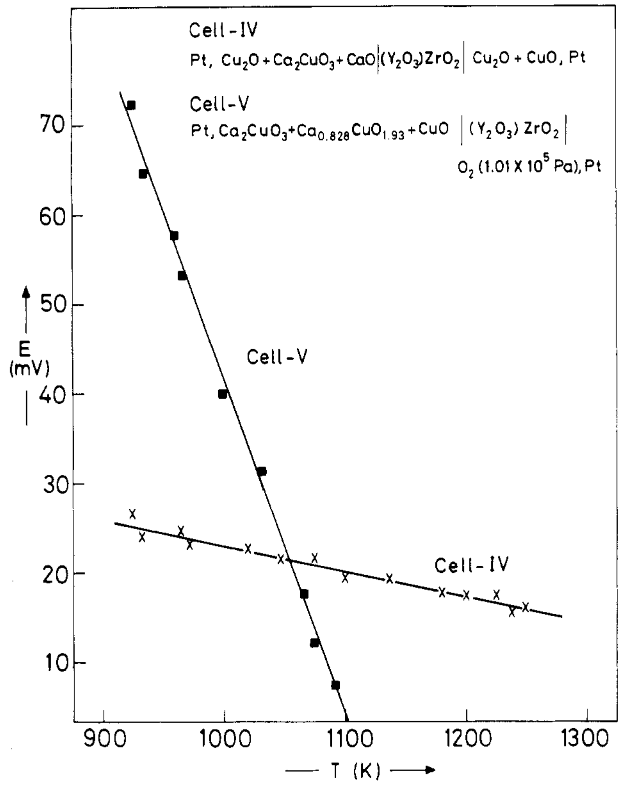

Figure 8. Temperature dependence of the emf of cell IV and V based on $(Y_2O_3)ZrO_2$ solid electrolyte.

$$\Delta\mu_{O_2}(CuO + Ca_2CuO_3 + Ca_{0.828}CuO_{1.93}) = -168\,670 + 152.6T(\pm 400)\ \mathrm{J\ mol^{-1}} \quad (4)$$

The standard Gibbs' energy of formation of the two ternary oxides from the component binary oxides and gaseous oxygen computed from the emf of galvanic cells employing an oxide electrolyte are summarized in Table III. It can be seen from Table III that Gibbs' energy of formation of ternary oxides derived from the two types of galvanic cells are in good agreement. There are only minor differences in the enthalpy and entropy terms, which are probably caused by uncertainties associated with the emf measurements. Thus the entire set of emf measurements involving five galvanic cells are internally consistent. It would be useful to confirm the thermodynamic data obtained in this study by calorimetric studies on enthalpy of formation and entropy of calcium cuprates.

4. Phase Relations as a Function of Partial Pressure of Oxygen. Using the thermodynamic data obtained in this study and auxiliary data from the literature,[17,18] the partial pressure of oxygen corresponding to several three-phase equilibria were computed at 873, 1073, and 1273 K. Since 1 mol of CuO gives 0.5 mol of Cu_2O or 1 mol of Cu on reduction, the number of moles of Cu remains unchanged when 1 mol of CuO, 0.5 mol of Cu_2O, or 1 mol of Cu is chosen as one of the components. Hence, the composition of the ternary mixtures can be expressed in terms of CaO and CuO + $^1/_2Cu_2O$ + Cu. The computed oxygen potential diagrams at 873, 1073, and 1223 K are shown in Figures 9–11 respectively.

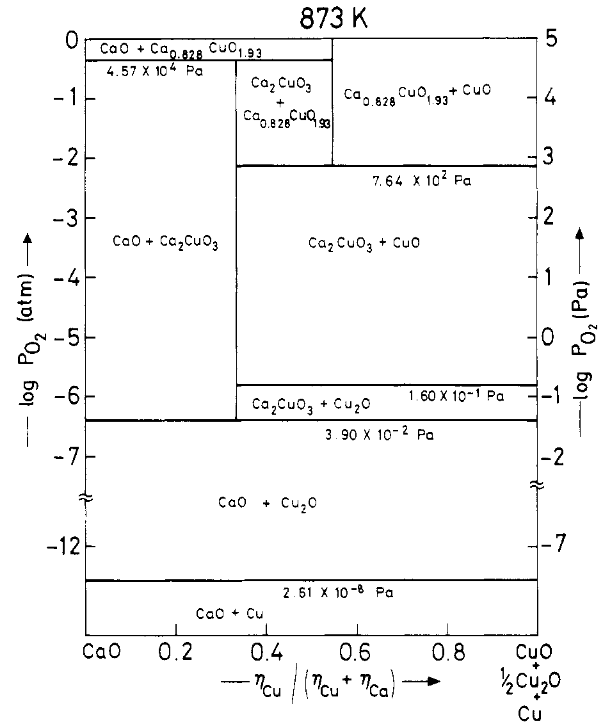

Figure 9. Isothermal representation of the phase relations in the system Ca–Cu–O at 873 K as a function of the partial pressure of oxygen, calculated from the results of this study.

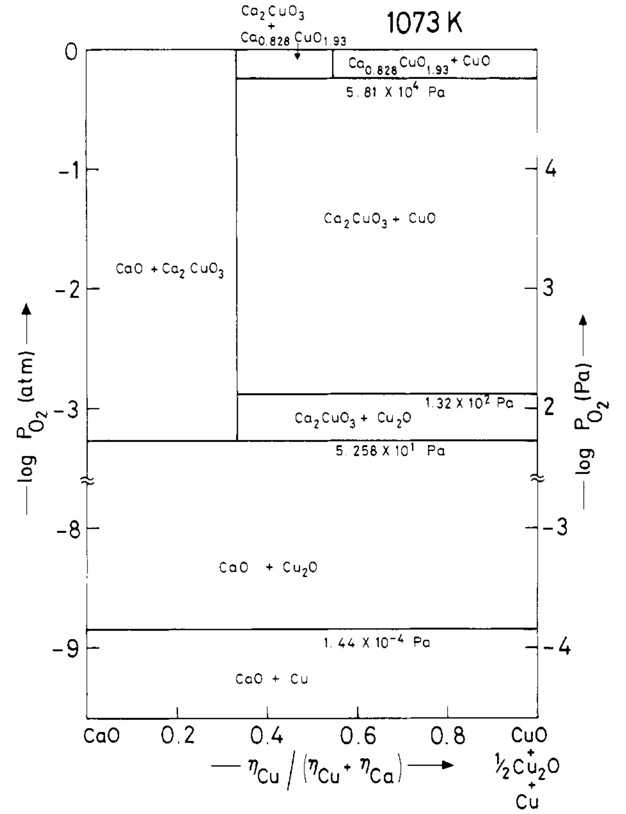

Figure 10. Isothermal section of the ternary system Ca–Cu–O, at 1073 K, as a function of the partial pressure of oxygen.

When three condensed phases and a gas phase are in equilibrium in a ternary system such as Ca–Cu–O, the system is monovariant. At a given temperature, the three condensed phases coexist at a unique partial pressure. The three-phase equilibria are therefore represented by horizontal lines in the oxygen potential diagram. It is seen that the topology of the diagram changes dramatically with temperature. It is interesting to note that at 873 K

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(17) Jacob, K. T.; Alcock, C. B. *J. Am. Ceram. Soc.* **1975**, *8*, 192.

(18) Jacob, K. T.; Jeffes, J. H. E. *Trans. Inst. Min. Met.* (sec. C: Mineral Process Extr. Metall.) 1971, *80*, C32.

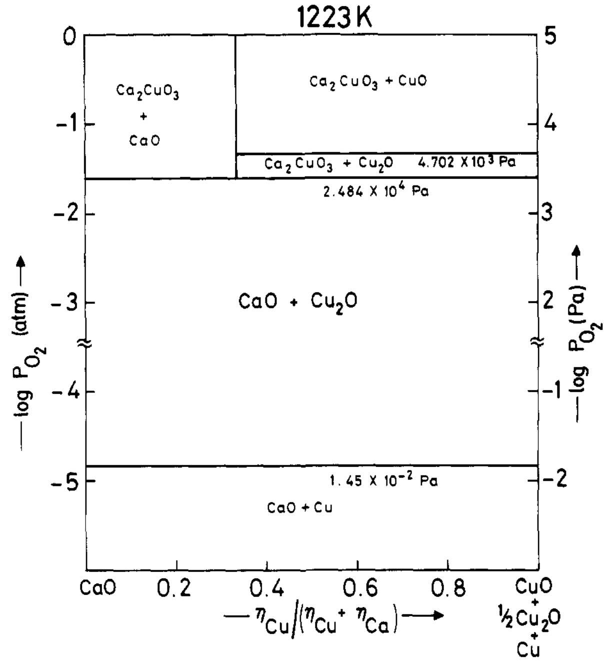

Figure 11. Phase relations in the ternary system Ca–Cu–O at 1223 K as a function of the partial pressure of oxygen.

the ternary phase Ca_2CuO_3 is unstable with respect to CaO and $Ca_{0.828}CuO_{1.93}$ above P_{O_2} = 4.57 × 10^4 Pa. At 1223 K, Ca_2CuO_3 appears as the only stable ternary phase. Phase relations at other temperatures and partial pressures of oxygen can be readily calculated from the thermodynamic data obtained in this study.

Summary

The phase diagram for the system Ca–Cu–O has been determined at 1073 and 1223 K. Two ternary oxides, Ca_2CuO_3 and $Ca_{0.828}CuO_{2-x}$, were identified at 1073 K. Only Ca_2CuO_3 is stable at 1223 K. There are no stable ternary phases containing copper in monovalent state. The oxygen content of $Ca_{0.828}CuO_{2-x}$, at 1073 K in pure oxygen and at an oxygen partial pressure corresponding to the three-phase field CuO + Ca_2CuO_3 + $Ca_{0.828}CuO_{2-x}$, was determined by analysis. The formula of the compound was determined as $Ca_{0.822}CuO_{1.93}$ or $Ca_{15}Cu_{18}O_{35}$. The Gibbs' energies of formation of the two ternary oxides were independently determined using solid-state galvanic cells incorporating either CaF_2 or $(Y_2O_3)ZrO_2$ as the solid electrolyte. Consistent results were obtained from both types of cells. They represent the only thermodynamic information now available on calcium cuprates.

A new variation of the emf technique has been employed to determine the oxygen content of $Ca_{0.828}CuO_{2-x}$. By measuring the emf of cells with a fluoride electrolyte and oxide electrodes as a function of the chemical potential of oxygen in the gas phase over the electrodes, the excess oxygen content of the oxide phase was evaluated, in good agreement with the analytical results. On the basis of the thermodynamic data obtained in this study and auxiliary data from the literature, phase relations in the system Ca–Cu–O have been evaluated at various temperatures, as a function of the partial pressure of oxygen.

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