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# Nonstoichiometry and Defect Structures in Copper Oxides and Ferrites

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The stoichiometry ranges of $Cu_2O_{1+y}$, $CuO_{1+y}$, $Cu_{0.984}Fe_{2.016}O_{4+y}$, $Cu_{1.011}Fe_{1.989}O_{4+y}$, and $Cu_{0.551}Fe_{2.449}O_{4+y}$ were established by high temperature electrochemical measurements in a stabilized zirconia electrolyte cell. The results were consistent with neutral oxygen vacancies for oxygen deficit and neutral cation vacancies for oxygen excess in cuprite, neutral oxygen vacancies in $Cu_{1.011}Fe_{1.989}O_{4+y}$ and $Cu_{0.551}Fe_{2.449}O_{4+y}$, neutral cation vacancies in $Cu_{0.984}Fe_{2.016}O_{4+y}$ and neutral associations of interstitial copper atoms in cupric oxide. The defect structures of these compounds were derived from the consideration of equilibrium with respect to oxygen between the solid and the gas phase. The absolute magnitudes of nonstoichiometry, defect concentrations and the enthalpy of defect formation were calculated. The enthalpies of the formation of Schottky defects in "$Cu_2O$" and "$CuFe_2O_4$" were calculated.

After the classic works of Wagner and Schottky (*1*) which established the connection between an imperfect crystal lattice and nonstoichiometry and which demonstrated the certainty of appearance of nonstoichiometry in any ionic crystal, the interest in determination of nonstoichiometry in oxides was intensified (*2–5*).

Reliable data relating chemical oxygen potentials to the temperature and composition of an oxide phase within its range of homogeneity are necessary in order to make the defect nature of the nonstoichiometry apparent and to obtain properties of the oxide systems. The method of coulometric titration in a high-temperature galvanic cell with a solid electrolyte is at present (*6–9*) extensively used for obtaining such data.

Cuprous oxide is the most investigated among oxide compounds of copper. Cuprite $Cu_2O_{1+\gamma}$ is a metal-deficient, *p*-type, extrinsic semiconductor whose properties are consistent with a structural model based on the presence of cation vacancies as the predominant ionic defects at sufficiently high temperatures and oxygen activities. Nonstoichiometry of cuprite was investigated by gas volumetric analysis (*10*), thermogravimetry (*11*), and chemical analysis of quenched samples (*12*). The data obtained are very inconsistent. The range of homogeneity of cuprous oxide includes compositions from $Cu_{1.996}O$ to $Cu_{1.9994}O$ at 1000°C (*10*), i.e., cuprous oxide in the equilibrium state is always metal deficient. According to the data of Wieder and Czanderna (*13*) this deficit is larger and extends to the composition $Cu_{1.5}O$. In Bloem's opinion (*14*) the range of homogeneity of the cuprite phase also includes compositions with deficient oxygen (at low oxygen activities). The measurements of Müser and Schilling (*15*), who detected electronic conduction in cuprous oxide in equilibrium with metallic copper, appears to corroborate this fact. The conclusions about the nature of the dominant defects are also not uniform. Dünnwald and Wagner's data (*10*) are interpreted within the framework of a model based on predominance of single-ionized copper vacancies and holes, whereas recent results of McKinzie and O'Keeffe (*16*) indicate neutral copper vacancies.

Data on nonstoichiometry in cupric oxide are not available. The independence of the conductivity of cupric oxide (*17*) of oxygen activity at high temperatures results from the significant intrinsic electronic excitation $O \rightleftarrows e' + h^{\cdot}$, and from a small contribution of nonstoichiometric defects, for example, $\frac{1}{2}O_2 \rightleftarrows O_O^{\times} + V_{Cu}'' + 2h^{\cdot}$.

The existence of two ferrite phases, $CuFeO_2$ and $Cu_xFe_{3-x}O_{4+\gamma}$, having an orthorhombic and spinel structure, respectively, have been discovered in the system Cu–Fe–O (*18*, *19*). It is possible to consider the last phase as an uninterrupted range of solid solutions of magnetite, $Fe_3O_{4+\gamma}$, and ferrite, $CuFe_2O_{4+\gamma}$ (*19*, *20*). Some authors (*21*) point out the necessity to single out the composition $Cu_{0.5}Fe_{2.5}O_{4+\gamma}$ as an independent compound which is correlated with a minimum in the Curie point, a maximum of lattice constant, and an extremal energy of activation for conductivity in the range $Fe_3O_4$–$CuFe_2O_4$. The character of nonstoichiometry dependence, ($\gamma$) *vs.* composition, temperature, and oxygen activity, is practically unknown. The largest value of $\gamma$ (*19*) in $Cu_{0.915}Fe_{2.085}O_{4+\gamma}$ at 1000°C is 0.042. Bergstein (*22*) points out the impossibility of producing the phase $Cu_{0.5}Fe_{2.5}O_{4+\gamma}$ with a negative value of $\gamma$ (at 1200°C, $0.01 \geqslant \gamma \geqslant 0$).

The purpose of the present work was to establish nonstoichiometry and the nature of the predominant defects *vs.* temperature and oxygen activity in oxides and ferrites of copper and to find out the real type of disorder in the indicated compounds.

## Experiment

### *Apparatus*

All experiments were carried out in a galvanic cell with the solid electrolyte $ZrO_2(CaO)$. The construction of a cell with an exactly fixed volume of the chamber used in the experiment is more advantageous than other types of construction since it allows for changing the oxygen content in the sample by coulometric titration under "*compensation conditions.*" This eliminates possible mistakes due to contact potential or leakage (*23*, *24*).

Two variants of a cell for temperature below and above 1000°C are shown in Figs. 1 and 2, respectively. The main details of the cell are a gastight alumina crucible of volume 0.5–1.5 $cm^3$ (in variant 1) and a Zircoa calcia-stabilized zirconia disk. The electrolyte disk was painted with platinum paste on the entire outer face and on that part of the inner face which would be within the enclosure; these electrodes were further prepared by being heated in air for 2 hr at 1100°C. Oxide powder was placed in the crucible and isolated from the outer gas space by a Pyrex ring having a low dissociation pressure. The chamber of the cell (in variant 2) was made of optical quartz, which reacts with the Pyrex ring at high temperatures and consequently assures the gastightness of a cell.

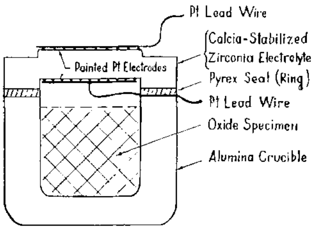

FIG. 1. The construction of the galvanic cell for coulometric titration involving an oxide specimen (variant 1).

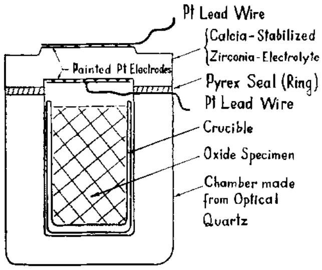

FIG. 2. The construction of the galvanic cell for coulometric titration (variant 2).

The apparatus (see Fig. 3) consists of the following parts:

1. *The vacuum part*—pumps, manometers and stopcocks, which permit smooth change of the total gas pressure and oxygen activity in the reactor;
2. *The heating system*—furnaces which keep the temperature of the cells constant to within ±0.5°C in a zone of 30–35 mm;
3. *The measuring system*—

a. calibrated Pt–Pt/Rh thermocouples, low-resistance potentiometer PPTN-1, reflecting gal-

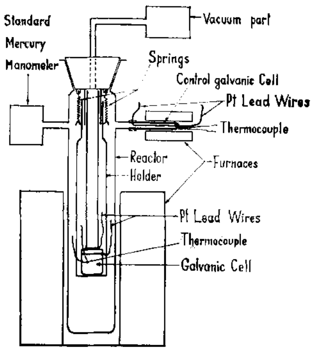

FIG. 3. The complete apparatus scheme for electrochemical investigation of nonstoichiometry in oxides.

vanometer M-101 to control temperature of the cells;

b. a high-resistance potentiometer P-304 and reflecting galvanometer M25/6 to measure the emf to within ±0.1 mV;

c. a control galvanic cell designed for measuring oxygen activities in the reactor [construction of a cell with the separated gas spaces is similar to the one described above (*25*)];

d. a standard mercury manometer to measure total gas pressure in the reactor to within ±0.1 Torr.

The electrical circuit scheme for coulometric titration is presented in Fig. 4.

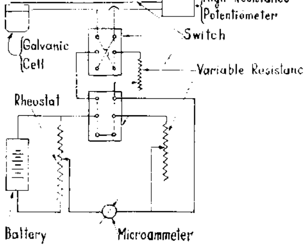

FIG. 4. The electric circuit scheme for coulometric titration.

### Procedure

The cell with a specimen is fixed in the holder (see Fig. 3) and placed in the reactor. The reactor is evacuated for a few hours to a residual pressure of ~$10^{-4}$ Torr at 100–200°C. Pure oxygen or a helium–oxygen mixture with a known oxygen activity is injected into the reactor. The gases are previously purified of possible impurities ($CO_2$, water vapor and others) before injection. Oxygen activity of the gas mixture is determined by the state of the specimen at the experimental temperature. Slow heating of the cell to 1000°C is carried out before the experiment to soften the Pyrex ring and to isolate the specimen from the outside gas space. Oxygen is removed from the chamber or admitted to it in known amounts by coulometric titration after reaching equilibrium in the system (the emf is constant and equal to zero if the oxygen activity of the outer gas electrode is equal to that of the inner gas electrode). At the same time, the oxygen activity in the reactor varies so that the emf would be near to zero, *i.e.*, the cell is kept in "*compensation conditions.*"

Because calcia-stabilized zirconia is a purely ionic conductor under the conditions of the experiments (*26*), the oxygen activity $P_{O_2}$ of the oxide specimen within the enclosure may be related to $P_{O_2}$ (ref) of the reference electrode by the voltage emf of the galvanic cell:

$$P_{O_2} = P_{O_2}(\mathrm{ref}) \cdot \exp\left(-\frac{4EF}{RT}\right). \qquad (1)$$

The oxygen activity $P_{O_2}$ (ref) of the gas electrode in the reactor is measured by a standard mercury manometer or by a control galvanic cell using the following equation

$$P_{O_2}(\mathrm{ref}) = 0.21\, P_{\mathrm{air}} \cdot \exp\left(-\frac{4E_i F}{RT_i}\right), \qquad (2)$$

where $E_i$ and $T_i$ are emf and temperature of the control cell respectively.

The number of moles of oxygen $\Delta n_{O_2}$ removed from or added to the enclosed electrode chamber by the passage of a current $J$ for a time $\tau$ is given by

$$\Delta n_{O_2} = \frac{J\tau}{4F} = \Delta n_{O_2}(\mathrm{sp}) - \Delta n_{O_2}(\mathrm{gas}). \qquad (3)$$

Through the use of the experimentally determined value for the volume of the gas phase in the enclosure, $\Delta n_{O_2}$(gas) is equal to $(V/RT) \cdot \Delta P_{O_2}$. The calculated values of $\Delta n_{O_2}$(gas) were then subtracted from $\Delta n_{O_2}$ to give $\Delta n_{O_2}$(sp) for the specimen. By knowing $g$, which is the mass of the oxide or ferrite specimen, $\Delta\gamma$, the change in oxygen nonstoichiometry of $MeO_{1+\gamma}$ or $Me_xFe_{3-x}O_{4+\gamma}$ could be calculated from

$$\Delta\gamma = \frac{2M}{g} \cdot \Delta n_{O_2}(\mathrm{sp}), \qquad (4)$$

where $M$ is the molecular weight of the specimen.

It is possible to expect that, for significant deviations from stoichiometry,

$$\gamma = K \cdot P_{O_2}^{1/n}, \qquad (5)$$

where $K$ is the proportionality constant, and the value of $n$ depends on the state of ionization of the atomic defects (*2*). Hence, for coulometric titration

$$\Delta\gamma = \gamma - \gamma(\mathrm{ref}) = K[P_{O_2}^{1/n} - P_{O_2}^{1/n}(\mathrm{ref})]. \qquad (6)$$

If Eqs. (4), (5), and (6) are combined, one obtains

$$\Delta\gamma = \frac{2M}{g}\left[\frac{J\tau}{4F} - \Delta n_{O_2}(\mathrm{gas})\right] \simeq K[P_{O_2}^{1/n} - P_{O_2}^{1/n}(\mathrm{ref})]. \qquad (7)$$

It is possible to select such a value of $n$ that $\Delta\gamma$ *vs.* $[\Delta(P_{O_2}^{1/n})]$ would be linear—that is, $K = \mathrm{const}$. This value of $K$, which (together with $n$) permits estimation of the absolute value of nonstoichiometry *vs.* oxygen activity, is determined by the slope of the line $\Delta\gamma = K[\Delta(P_{O_2}^{1/n})]$. If experimental data are not linear according to Eq. (6) because of two different values of $n$, the equation,

$$\gamma = K_1 P_{O_2}^{1/n} + K_2 P_{O_2}^{1/m}, \tag{8}$$[1]

is used. Here $n$ and $m$ are constants which depend on the nature of the atomic defects.

Thus

$$\Delta\gamma = K_1\,[\Delta(P_{O_2}^{1/n})] + K_2\,[\Delta(P_{O_2}^{1/m})], \tag{9}$$

or

$$\frac{\Delta(P_{O_2}^{1/n})}{\Delta\gamma} = \frac{1}{K_1} - \frac{K_2}{K_1}\cdot\frac{\Delta(P_{O_2}^{1/m})}{\Delta\gamma}. \tag{10}$$

The dependence of $\Delta(P_{O_2}^{1/n})/\Delta\gamma$ *vs.* $\Delta(P_{O_2}^{1/m})/\Delta\gamma$ is a line which has slope $K_2/K_1$ and intercept $1/K_1$ on the abscissa.

## Preparation of the Samples

Metallic copper with a total impurity content less than 30 ppm has been used as the starting material for the preparation of cupric oxide. The copper was dissolved in nitric acid, and the resulting copper nitrate was decomposed at 850–900°C, heated to 1050°C, and fired in oxygen for 3–4 hr.

Cuprous oxide near stoichiometry was prepared from cupric oxide by heating in a vacuum (~0.1 Torr) at 950°C for 5 hr and quenching.

Copper ferrites were prepared by thermal decomposition of solid solutions of the salts, $(Cu_xFe_{3-x})_{1/3}SO_4\cdot(NH_4)_2SO_4\cdot 6H_2O$, synthesized by the method of isothermal controlled supersaturation (*27*). The sulfates of copper, iron, and ammonium (special purity) were used for the synthesis of a solid solution of the salts. The thermal decomposition of the salts was carried out in air at 1000°C for 24 hr in order to prepare polycrystalline samples in the form of thin sheets, 0.5 to 1 mm thick.

On the basis of chemical analysis the ferrites synthesized are characterized by the following ratios (correct to ±0.005): Fe:Cu = 2.050; 1.965; and 4.445. These ratios correlate with the following formulas: $Cu_{0.984}Fe_{2.016}O_{4+\gamma}$; $Cu_{1.011}Fe_{1.989}O_{4+\gamma}$; and $Cu_{0.551}Fe_{2.449}O_{4+\gamma}$; respectively. X-Ray analysis showed all the ferrites to be single phase spinel.

## Results

*Cuprous oxide.* The examination of cuprite was carried out at 950, 1000, and 1050°C. These temperatures were chosen to minimize absorption effects and to accelerate attainment of equilibrium. The isothermal runs were made both in high-$P_{O_2}$ (30–1 Torr) and low-$P_{O_2}$ ($1–1\times10^{-3}$ Torr) ranges. Experimental data are presented in Table I.

Plots of $\Delta\gamma$ *vs.* $[P_{O_2}^{1/n}-P_{O_2}^{1/n}(\text{ref})]$ were constructed for estimating the constant $K$ in Eq. (6). The absolute value of the nonstoichiometry was obtained using Eq. (5). Analysis of such relations with different values of $n$ and application of the method of least squares show that the experimental data fit the following equations:

a. high-$P_{O_2}$ range

$$\gamma = 2.9\cdot\exp\left(-\frac{17\,500\pm4700}{RT}\right)\cdot P_{O_2}^{1/4}, \tag{11}$$

b. low-$P_{O_2}$ range

$$\gamma = -4.32\times10^4\cdot\exp\left(-\frac{54700\pm8000}{RT}\right)\cdot P_{O_2}^{-1/2}. \tag{12}$$

The values of $\gamma$ calculated from Eq. (11) are in good accord with the data of Wagner and Hammen (*12*) and O'Keeffe and Moore (*11*) (see Table II).

As follows from the theory of disorder (*2*), $n = 4$ is possible in Eq. (5) if the point defects are produced by the following quasichemical reactions:

$$\tfrac{1}{2}O_2 \rightleftarrows O_O^{\times} + 2V_{Cu}^{\times}, \tag{13}$$

or

$$\tfrac{1}{2}O_2 \rightleftarrows O_i' + h^{\cdot}. \tag{14}$$

Here, as in the notation of Kröger (*2*), the symbol identifies the defect, its subscript gives its location, and its superscript gives its charge state (crosses, primes, and dots representing neutral, negative, and positive charges, respectively).

In fact, as follows from the law of mass action,

$$K_{13} = [V_{Cu}^{\times}]^2\cdot P_{O_2}^{-1/2} \text{ and } K_{14} = [O_i']\cdot P\cdot P_{O_2}^{-1/2}.$$

Therefore:

$$\gamma \simeq \tfrac{1}{2}[V_{Cu}^{\times}] \propto P_{O_2}^{1/4}, \tag{15}$$

or

$$\gamma \simeq [O_i'] \simeq P \propto P_{O_2}^{1/4}, \tag{16}$$

respectively.

Since cuprous oxide is characterized by large deviations from stoichiometry (see Table II), the experimental data favor neutral copper vacancies

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[1] As follows from the theory of disorder (*2*), it is possible to expect such a dependence for solid phases that have nonstoichiometry due to two types of atomic defects having commensurable concentrations.

TABLE I

THE CHANGE OF NONSTOICHIOMETRY IN CUPROUS OXIDE

| Wt of specimen (g) | Vol of chamber (cm³) | Temp (°C) | Cell emf (mV) | Reference oxygen pressure (Torr) | $\frac{J\tau}{4F} \times 10^6$ (moles $O_2$) | Oxygen activity into chamber (Torr) | Change of nonstoichiometry $\Delta y \times 10^5$ |
|---|---|---|---|---|---|---|---|
| 2.1357 | 0.535 | 950 | − 59.7 | 3.06 | — | 29.5 | — |
| | | | − 53.0 | | 0.509 | 22.9 | 6.2 |
| | | | − 34.7 | | 1.843 | 11.4 | 23.0 |
| | | | − 19.6 | | 2.446 | 6.44 | 30.6 |
| | | | − 1.8 | | 3.109 | 3.27 | 39.2 |
| | | | 2.6 | | 3.367 | 2.77 | 42.6 |
| | | | 10.5 | | 3.618 | 2.05 | 45.9 |
| | | | 15.5 | | 3.882 | 1.70 | 49.4 |
| | | | 21.3 | | 4.279 | 1.36 | 54.7 |
| | | | 31.0 | | 4.693 | 0.944 | 60.2 |
| | | 1000 | − 67.8 | 3.08 | — | 36.5 | — |
| | | | − 55.1 | | 1.263 | 23.0 | 15.7 |
| | | | − 46.2 | | 1.706 | 17.0 | 21.1 |
| | | | − 34.9 | | 2.635 | 11.0 | 33.0 |
| | | | − 26.7 | | 3.154 | 8.16 | 39.7 |
| | | | − 17.8 | | 3.758 | 5.90 | 47.6 |
| | | | − 6.9 | | 4.398 | 3.96 | 56.0 |
| | | 1050 | − 48.3 | 3.16 | — | 17.2 | — |
| | | | − 40.7 | | 0.332 | 13.2 | 4.1 |
| | | | − 37.1 | | 0.470 | 11.6 | 5.8 |
| | | | − 33.4 | | 0.748 | 10.2 | 9.4 |
| | | | − 24.6 | | 0.988 | 7.50 | 12.4 |
| | | | − 22.7 | | 1.215 | 7.02 | 15.4 |
| | | | − 19.8 | | 1.773 | 6.32 | 28.2 |
| | | | − 5.0 | | 2.864 | 3.76 | 37.2 |
| | | | 10.2 | | 3.553 | 2.21 | 46.3 |
| | | | 13.0 | | 4.472 | 2.00 | 58.6 |
| 1.4528 | 1.492 | 950 | −131.0 | 0.824 | — | $5.71 \times 10^{-3}$ | — |
| | | | −112.8 | | 3.264 | $1.14 \times 10^{-2}$ | 64.3 |
| | | | −107.7 | | 4.665 | $1.38 \times 10^{-2}$ | 91.9 |
| | | | − 87.3 | | 6.528 | $3.00 \times 10^{-2}$ | 128.6 |
| | | | − 74.1 | | 8.391 | $4.95 \times 10^{-2}$ | 165.3 |
| | | | − 69.1 | | 10.260 | $5.99 \times 10^{-2}$ | 202.1 |
| | | 1000 | − 94.3 | 0.953 | — | $3.06 \times 10^{-2}$ | — |
| | | | − 77.5 | | 2.797 | $5.65 \times 10^{-2}$ | 55.1 |
| | | | − 59.7 | | 6.061 | $1.08 \times 10^{-1}$ | 119.4 |
| | | | − 37.9 | | 10.412 | $2.39 \times 10^{-1}$ | 205.1 |
| | | 1050 | − 88.6 | 1.109 | — | $4.02 \times 10^{-2}$ | — |
| | | | − 77.6 | | 5.442 | $5.93 \times 10^{-2}$ | 107.2 |
| | | | − 62.4 | | 9.798 | $1.01 \times 10^{-1}$ | 193.0 |
| | | | − 49.5 | | 14.250 | $1.59 \times 10^{-1}$ | 280.7 |
| | | | − 25.5 | | 18.600 | $3.69 \times 10^{-1}$ | 366.4 |
| | | | − 2.4 | | 22.565 | $8.28 \times 10^{-1}$ | 444.5 |

TABLE II

THE DEVIATION FROM STOICHIOMETRY IN CUPRITE $Cu_2O_{1+\gamma}$

| | $\gamma \times 10^3$ | | | | | |
|---|---|---|---|---|---|---|
| | From Ref. (*11*) | | From Ref. (*12*) | | Calc from Eq. (*11*) | |
| $P_{O_2}$ (Torr) | (°C): 900 | 1000 | 900 | 1000 | 900 | 1000 |
| 33 | — | 0.91 | — | 1.14 | 0.73 | 1.31 |
| 6.5 | 0.28 | 0.59 | 0.54 | 0.83 | 0.46 | 0.87 |
| 0.73 | 0.16 | 0.32 | 0.30 | 0.52 | 0.28 | 0.51 |

as the predominant defects in the lattice for the high-$P_{O_2}$ range (30–1 Torr). A large deviation from stoichiometry according to Eq. (14) is unlikely, due to crystal-chemistry considerations.

From Eqs. (11) and (15) it follows that

$$[V_{Cu}^{\times}] = 5.81 \cdot \exp\left(-\frac{17\,500 \pm 4700}{RT}\right) \cdot P_{O_2}^{1/4}, \qquad (17)$$

that is, the enthalpy of formation of cation vacancies with respect to oxygen gas at 1 atm corresponds to $\Delta H_{V_{Cu}^{\times}} = 17.5 \pm 4.7$ kcal mole$^{-1}$.

As can be seen from Eq. (12) for the low-$P_{O_2}$ range of stability of cuprite, $n = -2$. The theory of disorder (*2*) points out the possibility of such a value of $n$ if the defects are produced by the following quasichemical reaction[2]

$$O_O{}^{\times} \rightleftarrows \tfrac{1}{2}O_2 + V_O{}^{\times}, \qquad (18)$$

$$K_{18} = [V_O{}^{\times}] \cdot P_{O_2}^{1/2}. \qquad (19)$$

Then

$$[V_O{}^{\times}] \propto P_{O_2}^{-1/2}, \qquad (20)$$

Eq. (12), and condition $-\gamma = [V_O{}^{\times}]$ lead to

$$[V_O{}^{\times}] = 4.32 \times 10^4 \exp\left(-\frac{54\,700 \pm 8000}{RT}\right) \cdot P_{O_2}^{-1/2}, \qquad (21)$$

which corresponds to an enthalpy of formation of anion vacancies with respect to oxygen gas at 1 atm given by $\Delta H_{V_O{}^{\times}} = 54.7 \pm 8.0$ kcal mole$^{-1}$. Combining Eqs. (13) and (18), we obtain the equilibrium constant for the reaction

$$O \rightleftarrows V_O{}^{\times} + 2V_{Cu}^{\times} \qquad (22)$$

$$K_S = [V_O{}^{\times}] \cdot [V_{Cu}^{\times}]^2 = 1.46 \times 10^6 \exp\left(-\frac{89\,600 \pm 13\,400}{RT}\right), \qquad (23)$$

where the enthalpy of the formation of Schottky defects is given by $\Delta H_S = 89.6 \pm 13.4$ kcal mole$^{-1}$. This value is in good agreement with $\Delta H_S = 91$ kcal mole$^{-1}$ which was obtained by Bloem (*14*) through analysis of the optical spectrum of cuprous oxide. By using oxygen activity data (*28*) for both the Cu–$Cu_2O$ and $Cu_2O$–CuO two-phase equilibria,

$$\log P_{O_2} = 7.56 - \frac{17\,390}{T}, \qquad (24)$$

and

$$\log P_{O_2} = 9.02 - \frac{12\,730}{T}, \qquad (25)$$

respectively, and by extrapolating the curves described by Eqs. (11) and (12), one can estimate the range of homogeneity of cuprite (see Table III). Equations (11) and (12) allow one to establish the oxygen activities vs. temperature for exact stoichiometric cuprite:

$$\log P_{O_2} = 5.56(\pm 2.50) - \frac{10\,800 \pm 2500}{T}. \qquad (26)$$

Equations (11), (12), and (24)–(26) were used to establish the deviation from stoichiometry $\gamma$

TABLE III

OXYGEN NONSTOICHIOMETRY IN CUPRITE IN EQUILIBRIUM WITH (a) CUPRIC OXIDE AND (b) METALLIC COPPER

| | $\gamma \times 10^3$ in $Cu_2O_{1+\gamma}$ | | |
|---|---|---|---|
| | a | | b |
| $t$ (°C) | From Ref. (*11*) | Calc from Eq. (*11*) | Calc from Eq. (*12*) |
| 950 | 0.62 | 0.98 | −16.3 |
| 1000 | 1.15 | 1.64 | −20.6 |
| 1050 | 2.00 | 2.64 | −25.8 |

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[2] In this case, the formation of associated interstitial copper ions, for example, $2Cu_{Cu}^{\times} + O_O{}^{\times} \leftrightarrows \tfrac{1}{2}O_2 + (Cu_i)_2{}^{\times}$ is disregarded.

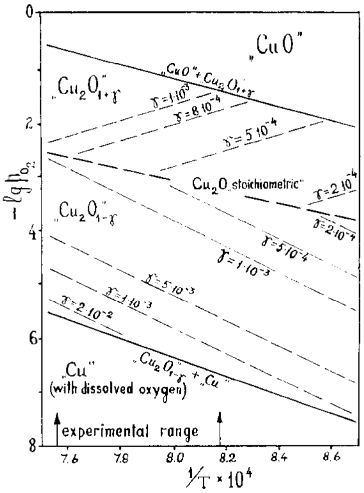

FIG. 5. $P_{O_2}$, $T$ diagram for cuprite.

in the whole cuprite field. Figure 5, in which it was supposed that Eqs. (13) and (18) are predominant down to two-phase boundaries $Cu_2O$–$CuO$ and $Cu$–$Cu_2O$, respectively, shows the result.

*Cupric oxide.* The examination of cupric oxide was carried out at 1072, 1100, and 1115°C. Isothermal runs were made from 340 to 1520 Torr. The experimental data represented in Table IV are described by the equation:

$$\gamma = -5.46 \times 10^{54} \cdot \exp\left(-\frac{365\,500 \pm 20\,000}{RT}\right) \cdot P_{O_2}^{-2}. \tag{27}$$

As follows from the theory of disorder (*2*), $n = -\frac{1}{2}$ is possible in Eq. (5) if point defects are produced by the following quasichemical reactions:

$$4O_O^{\times} \rightleftarrows 2O_2 + (V_O)_4^{\times}, \tag{28}$$

or

$$4Cu_{Cu}^{\times} + 4O_O^{\times} \rightleftarrows 2O_2 + (Cu_i)_4^{\times}. \tag{29}$$

In our opinion, the last one is more preferable, although direct data confirming such disorder

TABLE IV

THE CHANGE OF NONSTOICHIOMETRY IN CUPRIC OXIDE $CuO_{1+\gamma}$

| Wt of specimen (g) | Vol of cell chamber (cm³) | Temp of experiment (°C) | emf of the cell (mV) | Reference oxygen pressure $P_{O_2}$ (ref) (Torr) | Oxygen molecules removed from chamber $\frac{J_T}{4F} \times 10^6$ | Oxygen activity into chamber $P_{O_2}$ (Torr) | $P_{O_2}^{-2}$ (atm⁻²) | Change of nonstoichiometry $\Delta\gamma \times 10^6$ |
|---|---|---|---|---|---|---|---|---|
| 1.1010 | 0.502 | 1072 | −2.7 | 731.5 | — | 666.4 | 1.30 | — |
| | | | −2.4 | 649.0 | 0.39 | 596.9 | 1.62 | −4 |
| | | | 1.0 | 558.4 | 0.78 | 578.6 | 1.72 | 36 |
| | | | 2.0 | 450.3 | 1.16 | 483.3 | 2.47 | 10 |
| | | | 3.6 | 396.5 | 1.55 | 449.0 | 2.87 | 37 |
| | | | 1.1 | 396.5 | 1.94 | 412.2 | 3.40 | 61 |
| | | | 3.8 | 297.1 | 2.72 | 338.8 | 5.03 | 110 |
| 3.8130 | 1.106 | 1100 | 10.4 | 752.7 | — | 1070 | 0.50 | — |
| | | | 9.0 | 754.1 | 0.76 | 1022 | 0.55 | 6 |
| | | | 6.2 | 753.2 | 2.62 | 929.0 | 0.67 | 33 |
| | | | 4.6 | 723.9 | 5.42 | 845.9 | 0.81 | 105 |
| | | | 3.0 | 720.0 | 8.68 | 796.9 | 0.91 | 215 |
| | | | 4.2 | 516.8 | 18.00 | 596.6 | 1.62 | 496 |
| | | | 12.9 | 351.4 | 27.33 | 543.6 | 1.95 | 857 |
| | | | 4.3 | 350.5 | 36.65 | 405.4 | 3.51 | 1171 |
| 1.1010 | 0.502 | 1115 | 21.9 | 731.0 | — | 1523 | 0.24 | — |
| | | | 21.5 | 731.4 | 0.39 | 1503 | 0.25 | 39 |
| | | | 20.1 | 733.7 | 1.16 | 1438 | 0.28 | 97 |
| | | | 17.6 | 731.8 | 2.33 | 1317 | 0.33 | 164 |
| | | | 15.2 | 732.3 | 3.50 | 1218 | 0.39 | 249 |
| | | | 13.7 | 732.0 | 4.66 | 1157 | 0.43 | 367 |
| | | | 12.2 | 732.5 | 5.83 | 1101 | 0.48 | 489 |

TABLE V

THE CHANGE OF NONSTOICHIOMETRY IN COPPER FERRITE $Cu_{0.984}Fe_{2.016}O_{4+\gamma}$ WEIGHT OF SPECIMEN 1.3190 g; VOLUME OF CELL CHAMBER 1.093 cm$^3$

| Temp of experiment (°C) | emf of the cell (mV) | emf of the control cell (mV) | Temp of the control cell (°C) | $P_{air}$ (Torr) | Oxygen moles admitted to chamber $\frac{J_T}{4F}\times 10^6$ (moles of $O_2$) | Oxygen activity chamber $P_{O_2}$ (Torr) | $P_{O_2}^{2/3}$ (atm$^{2/3}$) | Change of nonstoichiometry $\Delta\gamma \times 10^3$ |
|---|---|---|---|---|---|---|---|---|
| 1000 | 33.2 | −146.4 | 890 | 746.8 | — | 1.5 | 0.016 | — |
| | 9.7 | −109.0 | 896 | 741.8 | 2.72 | 2.0 | 0.025 | 0.7 |
| | − 2.5 | − 84.9 | 910 | 741.4 | 6.48 | 5.0 | 0.035 | 1.6 |
| | −25.5 | − 45.5 | 859 | 741.0 | 12.04 | 10.0 | 0.056 | 3.2 |
| | −22.9 | − 39.0 | 902 | 741.5 | 15.33 | 10.1 | 0.056 | 4.1 |
| | −27.7 | − 21.5 | 896 | 743.3 | 22.80 | 24.6 | 0.100 | 6.1 |
| | −28.0 | − 16.8 | 888 | 741.5 | 29.38 | 28.6 | 0.112 | 7.9 |
| | −38.7 | 0.0 | 891 | 741.8 | 37.63 | 38.0 | 0.136 | 10.1 |
| 1050 | 55.8 | −146.0 | 892 | 746.7 | — | 3.2 | 0.026 | — |
| | 31.2 | −108.5 | 902 | 741.2 | 2.72 | 6.4 | 0.041 | 0.7 |
| | 18.7 | − 85.8 | 910 | 740.9 | 6.48 | 10.5 | 0.058 | 1.6 |
| | − 5.5 | − 44.0 | 891 | 740.6 | 12.04 | 21.0 | 0.091 | 3.2 |
| | − 3.0 | − 49.0 | 901 | 742.0 | 15.33 | 21.0 | 0.091 | 4.1 |
| | − 8.1 | − 21.0 | 894 | 743.0 | 22.80 | 49.9 | 0.163 | 6.0 |
| | − 8.6 | − 24.0 | 896 | 741.6 | 29.38 | 59.7 | 0.183 | 7.8 |
| | −20.2 | 0.0 | 894 | 747.0 | 37.63 | 77.2 | 0.218 | 9.8 |
| 1100 | 80.3 | −123.0 | 898 | 746.8 | — | 6.9 | 0.044 | — |
| | 55.0 | −107.0 | 904 | 740.6 | 2.72 | 13.7 | 0.069 | 0.7 |
| | 39.3 | − 98.5 | 892 | 738.9 | 6.48 | 20.6 | 0.090 | 1.5 |
| | 13.4 | − 55.5 | 892 | 740.4 | 12.04 | 40.0 | 0.140 | 3.2 |
| | 17.1 | − 47.5 | 905 | 742.2 | 15.33 | 41.4 | 0.144 | 4.0 |
| | 9.0 | − 21.5 | 893 | 742.2 | 22.80 | 90.0 | 0.241 | 5.9 |
| | 7.1 | − 16.0 | 909 | 741.8 | 29.38 | 105.7 | 0.268 | 7.6 |
| | − 5.6 | 0.0 | 890 | 751.2 | 37.63 | 130.6 | 0.309 | 9.8 |
| | 1.1 | 0.0 | 874 | 752.6 | 46.40 | 164.0 | 0.360 | 12.1 |

are absent. From Eq. (27), we obtain the enthalpy of formation of $(Cu_i)_4{}^{\times}$ with respect to oxygen gas at 1 atm $\Delta H_{(Cu_i)_4{}^{\times}} = 366 \pm 20$ kcal mole$^{-1}$.

*Ferrite with copper deficit.* The examination of the ferrite $Cu_{0.984}Fe_{2.016}O_{4+\gamma}$ was carried out at 1000, 1050, and 1100°C from 1 to 165 Torr. The experimental data shown in Table V and treated by the method of least squares for different values of $n$ and $m$ are described by the equation

$$\gamma = 1.72 \times 10^{-6}\cdot\exp\left(\frac{27\,900 \pm 3500}{RT}\right)\cdot P_{O_2}^{2/3}. \qquad (30)$$

As follows from the theory of disorder (*2*), $n = \frac{3}{2}$ is possible in Eq. (5) if the point defects would be produced by the reaction

$$2O_2 \rightleftarrows 4O_O{}^{\times} + 3V_M{}^{\times}. \qquad (31)^{[3]}$$

In fact, from the law of mass action

$$K_{31} = [V_M{}^{\times}]^3\cdot P_{O_2}^{-2}, \qquad (32)$$

it follows that

$$\gamma = \tfrac{4}{3}[V_M{}^{\times}] \propto P_{O_2}^{2/3}. \qquad (33)$$

Equations (30), (32), and (33) allow us to establish the equilibrium constant of Eq. (31):

$$K_{31}^{1/3} = 1.29 \times 10^{-6}\cdot\exp\left(\frac{27\,900 \pm 3500}{RT}\right). \qquad (34)$$

---

[3] This reaction takes into account that $[M]_{tot}/[O]_{tot}$ is equal to $\frac{3}{4}$ in stoichiometric spinel and production of cation vacancies in *A*- or *B*-positions requires equal energy at high temperatures.

TABLE VI

THE CHANGE OF NONSTOICHIOMETRY IN COPPER FERRITE $Cu_{1.011}Fe_{1.989}O_{4+\gamma}$

| Temp of experiment (°C) | emf of the cell (mV) | Reference oxygen pressure $P_{O_2}$ (ref) (Torr) | Oxygen moles admitted to chamber $\frac{J_T}{4F} \times 10^6$ (moles of $O_2$) | Oxygen activity into chamber $P_{O_2}$ (Torr) | $P_{O_2}^{-1/2}$ ($atm^{-1/2}$) | Change of nonstoichiometry $\Delta\gamma \times 10^3$ |
|---|---|---|---|---|---|---|
| 1000 | 23.6 | 24.1 | — | 57.1 | 3.65 | — |
| | 17.1 | 33.8 | 39.4 | 63.0 | 3.47 | 10.7 |
| | 11.6 | 45.7 | 69.1 | 69.7 | 3.30 | 18.9 |
| | 7.4 | 56.6 | 95.3 | 74.0 | 3.20 | 26.0 |
| | 6.6 | 58.4 | 117.0 | 74.3 | 3.20 | 31.9 |
| | 2.5 | 85.2 | 136.3 | 93.4 | 2.85 | 37.2 |
| | 2.1 | 93.0 | 151.8 | 100.3 | 2.75 | 41.4 |
| | 1.7 | 97.0 | 162.2 | 103.3 | 2.71 | 44.2 |
| 1050 | 1.0 | 72.8 | — | 75.3 | 3.18 | — |
| | −3.9 | 98.5 | 31.1 | 85.9 | 1.98 | 8.5 |
| | 0.0 | 96.9 | 63.2 | 97.0 | 2.80 | 17.2 |
| | −2.0 | 116.2 | 89.9 | 108.2 | 2.65 | 24.5 |
| | −5.2 | 141.6 | 111.4 | 118.1 | 2.54 | 30.4 |
| | −2.0 | 140.5 | 138.7 | 131.0 | 2.41 | 37.8 |
| | −3.0 | 163.4 | 162.6 | 146.9 | 2.28 | 44.3 |
| | −4.3 | 186.5 | 181.8 | 160.6 | 2.18 | 49.5 |
| | −1.6 | 185.8 | 201.2 | 175.7 | 2.08 | 54.8 |
| | −1.7 | 205.0 | 219.6 | 192.9 | 1.98 | 59.8 |
| | −1.3 | 229.6 | 238.0 | 219.4 | 1.86 | 64.7 |
| 1100 | 3.3 | 72.9 | — | 81.5 | 3.05 | — |
| | 10.0 | 72.8 | 75.8 | 102.3 | 2.73 | 20.6 |
| | 6.0 | 99.2 | 145.3 | 121.5 | 2.50 | 39.7 |
| | 5.0 | 119.3 | 206.0 | 141.3 | 2.32 | 56.2 |
| | 4.6 | 140.0 | 258.3 | 163.6 | 2.16 | 70.4 |
| | 6.5 | 150.9 | 294.0 | 188.0 | 2.01 | 80.0 |

*Ferrites with copper excess.* The examination of the ferrite $Cu_{1.011}Fe_{1.989}O_{4+\gamma}$ was made at 1000, 1050, and 1100°C from 57 to 220 Torr. The experimental data represented in Table VI and treated by the method of least squares show that $\log|\gamma|$ *vs.* $\log P_{O_2}$ is linear only when $n = -2$:

$$\gamma = -887 \cdot \exp\left(-\frac{25\,500 \pm 3700}{RT}\right) \cdot P_{O_2}^{-1/2}. \quad (35)$$

As follows from the theory of disorder (*2*), $n = -2$ is possible in Eq. (5) if the point defects are produced by the quasichemical reaction

$$O_O^\times \rightleftarrows \tfrac{1}{2}O_2 + V_O^\times, \quad (36)$$

whereupon

$$K_{36} = [V_O^\times] \cdot P_{O_2}^{1/2}. \quad (37)$$

We obtain from Eq. (37) that $\gamma \simeq [V_O^\times] \propto P_{O_2}^{-1/2}$. It is necessary to point out that there are no reactions describing oxygen deficit in copper ferrite by production of interstitial defects with $n = -2$. For example, $n$ is equal to $-\frac{3}{2}$, $-3$, and $-\frac{9}{2}$, respectively, for the following reactions:

$$3M_M^\times + 4O_O^\times \rightleftarrows 2O_2 + 3M_i^\times, \quad (38)$$

$$3M_M^\times + 4O_O^\times \rightleftarrows 2O_2 + 3M_i^\cdot + 3e' \quad (39)$$

$$3M_M^\times + 4O_O \rightleftarrows 2O_2 + 3M_i^{\cdot\cdot} + 6e'. \quad (40)$$

Equations (35) and (37) lead to:

$$k_{36} = 887 \cdot \exp\left(-\frac{25\,500 \pm 3700}{RT}\right). \quad (41)$$

TABLE VII

THE CHANGE OF NONSTOICHIOMETRY IN COPPER FERRITE $Cu_{0.551}Fe_{2.449}O_{4+\gamma}$ WEIGHT OF SPECIMEN 0.8832 g; VOLUME OF CELL CHAMBER 0.546 cm$^3$

| Temp of experiment (°C) | emf of the cell (mV) | Reference oxygen pressure $P_{O_2}$ (ref) (Torr) | Oxygen moles admitted to chamber $\frac{J_T}{4F} \times 10^6$ (moles of $O_2$) | Oxygen activity into chamber $P_{O_2}$ (Torr) | $P_{O_2}^{-1/2}$ (atm$^{-1/2}$) | Change of nonstoichiometry $\Delta\gamma \times 10^3$ |
|---|---|---|---|---|---|---|
| 900 | 6.0 | 3.2 | — | 4.1 | 13.68 | — |
| | 10.1 | 4.3 | 14.35 | 6.6 | 10.89 | 7.7 |
| | 0.2 | 8.2 | 23.95 | 8.3 | 9.59 | 12.8 |
| | 3.0 | 10.1 | 32.80 | 11.4 | 8.18 | 17.5 |
| | 0.0 | 18.8 | 41.55 | 18.8 | 6.36 | 22.2 |
| | 0.3 | 24.6 | 46.75 | 23.2 | 5.72 | 24.9 |
| | 0.0 | 33.1 | 50.10 | 33.1 | 4.79 | 26.7 |
| 950 | 1.2 | 21.3 | — | 22.2 | 5.84 | — |
| | 0.8 | 33.6 | 9.60 | 34.6 | 4.69 | 4.8 |
| | 0.4 | 49.0 | 18.42 | 49.7 | 3.91 | 9.5 |
| | 0.5 | 77.0 | 27.15 | 78.4 | 3.11 | 14.0 |
| | 0.4 | 106.0 | 32.35 | 107.8 | 2.66 | 16.6 |
| | 0.1 | 138.7 | 35.72 | 139.1 | 2.34 | 18.4 |
| | 0.4 | 225.3 | 39.27 | 229.2 | 1.82 | 20.0 |
| | 0.3 | 286.5 | 41.15 | 289.8 | 1.62 | 20.7 |
| 1000 | 2.6 | 46.1 | — | 50.7 | 3.87 | — |
| | 0.1 | 91.8 | 14.35 | 92.2 | 2.87 | 7.8 |
| | 0.7 | 134.3 | 23.95 | 137.6 | 2.35 | 13.0 |
| | 0.4 | 201.6 | 32.80 | 204.3 | 1.93 | 17.0 |
| | 0.7 | 292.8 | 41.55 | 300.4 | 1.59 | 21.3 |
| | 0.2 | 409.6 | 46.75 | 412.7 | 1.36 | 23.7 |
| | 0.3 | 482.7 | 50.10 | 487.6 | 1.25 | 25.2 |
| | 0.2 | 731.3 | 53.70 | 735.4 | 1.02 | 26.2 |

Having combined Eqs. (34) and (41) for reaction,

$$O \rightleftarrows 3V_M{}^\times + 4V_O{}^\times, \qquad (42)$$

we obtain

$$K_S = [V_O{}^\times]^4[V_M]^3 = K_{36}^4 K_{31}$$
$$= 1.32 \times 10^{-6}\cdot\exp\left(-\frac{18\,450 \pm 25\,300}{RT}\right), \qquad (43)$$

that is, the enthalpy of formation of Schottky defects in copper ferrite, $CuFe_2O_4$, is $\Delta H_S = 18.45 \pm 25.3$ kcal mole$^{-1}$. Equations (30) and (35) permit us to establish the temperature dependence of the oxygen activity for copper ferrite having exact stoichiometric composition of oxygen and the metals, $CuFe_2O_4$, as follows:

$$\log P_{O_2} = 7.47(\pm 1.95) - \frac{10\,000 \pm 1350}{T}. \qquad (44)$$

We have investigated the copper ferrite $Cu_{0.551}Fe_{2.449}O_{4+\gamma}$ which is near to $Cu_{0.5}Fe_{2.5}O_{4+\gamma}$. The coulometric titration was made at 900, 950, and 1000°C from 4 to 735 Torr. The experimental data shown in Table VII and treated by the method of least squares with different values of $n$ and $m$ in Eqs. (5) and (10) show that $\log|\gamma|$ *vs.* $\log P_{O_2}$ is linear only under the condition that $n = -2$:

$$\gamma = -5.82 \times 10^3\cdot\exp\left(-\frac{33\,750 + 5760}{RT}\right)\cdot P_{O_2}^{-1/2}. \qquad (45)$$

$n = -2$ indicates the predominance of neutral oxygen vacancies, which is expressed by

$$[V_O{}^\times] = 5.82 \times 10^3\cdot\exp\left(-\frac{33\,750 \pm 5760}{RT}\right)\cdot P_{O_2}^{-1/2}, \qquad (46)$$

that is, the enthalpy of formation of anion vacancies with respect to oxygen gas at one atm is given by $\Delta H_{V_O^x} = 33.8 \pm 5.8$ kcal mole$^{-1}$. This value of the enthalpy is larger than the one for ferrite with low copper deficit.

## Conclusions

1. High-temperature coulometric titration in a galvanic cell involving a stabilized zirconia electrolyte and an enclosed electrode chamber was used to establish the $P_{O_2}$-dependence of nonstoichiometry in copper oxides and ferrites.

2. These measurements corresponded to reasonable defect models which allowed calculation of the absolute magnitudes and $P_{O_2}$-dependences of defects in these compounds.

3. The principal defects in $Cu_2O_{1+\gamma}$ are neutral oxygen vacancies for oxygen deficit and neutral cation vacancies for oxygen excess; neutral oxygen vacancies are the predominant defects in $Cu_{1.011}Fe_{1.989}O_{4+\gamma}$ and $Cu_{0.551}Fe_{2.449}O_{4+\gamma}$; neutral cation vacancies dominate in $Cu_{0.984}Fe_{2.016}O_{4+\gamma}$, but neutral associations of interstitial copper atoms or associations of oxygen vacancies can dominate in cupric oxide.

4. Copper ferrite $CuFe_2O_4$ and cuprite show the Schottky type of disorder.

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