

Activities in the Spinel Solid Solution, Phase Equilibria and Thermodynamic Properties of Ternary Phases in the System Cu-Fe-O

K. T. JACOB, K. FITZNER, AND C. B. ALCOCK

A review of the structural and thermodynamic information and phase equilibria in the Cu-Fe-O system suggested that a consistent, quantitative description of the system is hampered by lack of data on activities in the spinel solid solution CuFe_2O_4 - Fe_3O_4 . Therefore the activity of Fe_3O_4 in this solid solution is derived from measurements of the oxygen potentials established at 1000°C by mixtures containing Fe_2O_3 and spinel solid solutions of known composition. The oxygen pressures were measured manometrically for solid solutions rich in CuFe_2O_4 , while for Fe_3O_4 -rich compositions the oxygen potentials were obtained by an emf technique. The activities show significant negative deviations from Raoult's law. The compositions of the spinel solid solutions in equilibrium with $\text{CuO} + \text{CuFeO}_2$ and $\text{Cu} + \text{CuFeO}_2$ were obtained from chemical analysis of the solid solution after magnetic separation. The oxygen potential of the three-phase mixture $\text{Cu} + \text{CuFeO}_2 + \text{Fe}_3\text{O}_4(\text{spinel s.s.})$ was determined by a solid oxide galvanic cell. From these measurements a complete phase diagram and consistent thermodynamic data on the ternary condensed phases, CuFeO_2 and CuFe_2O_4 , were obtained. An analysis of the free energy of mixing of the spinel solid solution furnished information on the distribution of cations and their valencies between the tetrahedral and octahedral sites of the spinel lattice, which is consistent with X-ray diffraction, magnetic and Seebeck coefficient measurements.

THE Cu-Fe-O system is of prime importance in the pyro- and hydrometallurgy of copper. Several workers¹ have suggested the existence of copper ferrites in mattes during smelting. Magnetite and other ferrite solid solutions have long been discussed as potential sources of copper loss in reverberatory and converter slags.² These compounds have also been sometimes found in the 'false bottom' formed in reverberatory furnaces.³ The copper ferrite that forms under certain conditions during the fluidized-bed roasting of copper sulphide concentrates⁴ is difficult to leach economically during hydrometallurgical processing of copper concentrates. The discrepancy that exists between the conditions for the formation of this ferrite during roasting predicted from available thermodynamic data⁵ and those observed in practice, suggest that the thermodynamic data for the ternary condensed phases may require revision. Because of its ferrimagnetic and semiconducting properties, copper ferrite and its solid solutions with other ferrites (*e.g.* ZnFe_2O_4) are of interest in the electronic industry,⁶ where a close control of the distribution of cations and their valencies between the tetrahedral and the octahedral sites of the spinel are required for obtaining the desired properties.

The importance of the Cu-Fe-O system has attracted the attention of researchers in mineralogy, ceramics, metallurgy and solid state physics and chemistry.

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Manuscript submitted December 2, 1976.

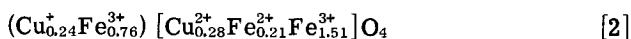
Yund and Kullerud⁷ have conducted the first extensive phase diagram investigation of this system at temperatures below 800°C by X-ray and metallographic examination of the equilibrated phases contained in evacuated silica capsules. They identified two ternary phases, delafossite (CuFeO_2) and cupric ferrite (CuFe_2O_4), in addition to the stable phases in the binary systems Cu-O and Fe-O. There was no evidence of a solid solution between the spinel phases CuFe_2O_4 and Fe_3O_4 . Another systematic investigation of phase relations was carried out by Gadalla and White,⁸ who measured the loss in weight of mixtures of $\text{CuO} + \text{Fe}_2\text{O}_3$ on heating from 800 to 1500°C, under oxygen partial pressures of 0.21 to 1 atm. They found increasing solid solubility between the two spinel phases CuFe_2O_4 and Fe_3O_4 with increasing temperature. More recent work by Schaefer *et al.*,⁹ in the temperature range 900 to 977°C and the oxygen partial pressure range from 10^{-4} to 0.5 atm, support the finding of solid solubility between the spinel phases. A new compound of the composition $\text{Cu}_6\text{Fe}_3\text{O}_7$, postulated by Gadalla and White⁸ to replace the compound delafossite, has not been identified by subsequent investigators.^{9,16,18,20,23,29}

The structure of CuFeO_2 is rhombohedral with $a = 5.96\text{\AA}$ and $\alpha = 29 \text{ deg } 6 \text{ min}$; or in the hexagonal description $a = 3.03\text{\AA}$, $c = 17.09\text{\AA}$. The iron has octahedral coordination, while copper has a linear two-fold oxygen coordination like in Cu_2O . The oxygen is surrounded by a tetrahedron of three iron and one copper.¹⁰ Pabst has argued on the basis of crystal ionic radii, and Delorme and Bertaut¹¹ have argued on the basis of an electrostatic calculation of the lattice energy that the iron in delafossite is present in the trivalent state and the copper in the monovalent state ($\text{Cu}^+\text{Fe}^{3+}\text{O}_2^-$). Muir and Wiedersich¹² have confirmed this valency assignment by Moessbauer studies. Jef-

erson¹³ has shown that the lattice parameter of $\text{CuFe}_2\text{O}_4\text{-Fe}_3\text{O}_4$ spinel solid solutions shows a maximum and the Curie temperature shows a minimum at the equimolar composition ($\text{Cu}_{0.5}\text{Fe}_{2.5}\text{O}_4$). For this reason some researchers^{14,15} have uncritically characterized this composition as a separate compound (CuFe_5O_8). As the iron concentration increases in the spinel solid solution, the Seebeck coefficient changes from positive to negative values at $\text{Cu}_{0.775}\text{Fe}_{2.225}\text{O}_4$.¹³ It was suggested that the equilibrium



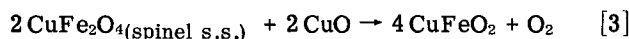
lies to the left up to this composition; at higher concentrations of iron some Fe^{2+} ions are present to control the conduction mechanism.¹³ Recently Červinka and Šimša¹⁶ have determined the distribution of copper and iron among the tetrahedral and octahedral sites in the spinel of the composition $\text{Cu}_{0.5}\text{Fe}_{2.5}\text{O}_4$ by X-ray diffraction. Further, based on their¹⁶ saturation magnetization measurements, site preference energies of cations and the Neel model of ferrimagnetism the following distribution of cations has been proposed:



where () denotes tetrahedral and [] denotes octahedral sites of the spinel lattice. The cupric ferrite and the spinel solid solutions rich in this component undergo cubic to tetragonal transformation at temperatures below 400°C (Ref. 9) due to cooperative Jahn-Teller effect of Cu^{2+} ion on the octahedral site.

The decomposition of the spinel solid solution at low temperatures by a eutectoid reaction to delafossite and hematite was first proposed by Bertaut and Delorme,¹⁷ disputed by Gadalla and White,⁸ but later confirmed by Wiedersich *et al.*,¹⁸ Yamaguchi and Shiraishi,¹⁹ and Šimša and Holba.²⁰ The temperature of the exothermic decomposition is $980 \pm 30^\circ\text{C}$ (Refs. 19, 20) for $\text{Cu}_{0.5}\text{Fe}_{2.5}\text{O}_4$. Almost all compositions of the $\text{CuFe}_2\text{O}_4\text{-Fe}_3\text{O}_4$ join underwent eutectoid decomposition on cooling by a process of nucleation and growth,²¹ yielding CuFeO_2 , Fe_2O_3 and either CuFe_2O_4 -rich or Fe_3O_4 -rich spinel solid solution depending on whether the Cu/Fe ratio is more or less than one-fifth. The phase diagrams suggested by Yund and Kullerud⁷ for low temperatures, showing the absence of solid solution between the two spinel phases, can thus be reconciled with the phase diagrams at higher temperatures,⁸ where the spinel solid solution is stable. A recent phase diagram suggested by Fredriksson and Rosén²³ for the Fe_3O_4 corner of the system Cu-O- Fe_3O_4 is in conformity with these findings. Based on a review of literature, Luraschi and Elliott²⁴ have composed a schematic representation of phase equilibria at 1300 and 1400°C, where copper and its oxides form liquid phases. Šimša and Holba²⁰ have also suggested a small effect of oxygen nonstoichiometry on the eutectoid decomposition. It was suggested²⁰ that δ in $\text{Cu}_{0.5}\text{Fe}_{2.5}\text{O}_{4+\delta}$ can have values from -0.013 to $+0.055$. By coulometric titration of oxygen through a solid electrolyte, Tretyakov *et al.*²² have studied the variation of δ with oxygen partial pressure in greater detail.

The variation of the oxygen potential with temperature for the three-phase equilibria,



measured in five different investigations^{9,25-28} are in good agreement. The results have been compared by Schaefer *et al.*,⁹ a least mean-squares analysis suggests the following equation,

$$\log p_{\text{O}_2} = \frac{-10,446}{T} + 7.438 \quad [4]$$

where the oxygen partial pressure is expressed in atmospheres. It was also shown⁹ that the delafossite is a stoichiometric compound and its solubility in cuprous oxide is negligible. The cupric ferrite in equilibrium with CuO and CuFeO_2 is a spinel solid solution whose composition has not been measured. More recently the oxygen potential over the three-phase mixture $\text{Cu} + \text{CuFeO}_2 + \text{Fe}_3\text{O}_4(\text{spinel s.s.})$ was measured by Paulsson *et al.*²⁹ using a solid oxide galvanic cell. The magnetite phase in equilibrium is reported to be a spinel solid solution in which the mole fraction of Fe_3O_4 is 0.87 ± 0.02 in the temperature range 700 to 1000°C.

Zalazinski *et al.*³⁰ have measured the $\text{H}_2/\text{H}_2\text{O}$ ratio corresponding to the reduction of CuFeO_2 to Cu and $\text{Fe}_3\text{O}_4(\text{spinel s.s.})$ from 700 to 1000°C. Navrotsky and Kleppa³¹ have measured the heat of formation of CuFe_2O_4 as $+5.1 \pm 0.2$ kcal/mole or $+21.13 \pm 0.8$ kJ/mole by high-temperature oxide-melt-solution calorimetry at 723°C. The copper ferrite used by them was prepared by heating CuO and Fe_2O_3 at 900°C in air for 90 h. Results of this study suggest that under these conditions, a heterogeneous mixture containing 4 to 6 pct CuO and a spinel solid solution rich in CuFe_2O_4 would result. The uncertainty in the calorimetric value may therefore be of the order of 1 kcal/mole or 4.2 kJ/mole.

In an earlier study^{32,33} it was shown that the entropy of formation of cubic spinels of the type $\text{M}^{2+}\text{X}_2^{3+}\text{O}_4$, from component oxides MO and X_2O_3 with rock-salt and corundum structures, can be expressed as $-1.75 + \Delta S^M + \Delta S_{\text{rand}}$ cal deg⁻¹ mole⁻¹ or $-7.25 + \Delta S^M + \Delta S_{\text{rand}}$ J deg⁻¹ mole⁻¹, where ΔS^M is the entropy of cation mixing in the tetrahedral and octahedral sites of the spinel and ΔS_{rand} is the Jahn-Teller entropy associated with the randomization of the orientation of orbitals with prolate or oblate distortions. From a study of the thermodynamics of formation of CuAl_2O_4 from CuO and $\alpha\text{-Al}_2\text{O}_3$, the entropy of the hypothetical transformation of CuO from the tenorite to rock-salt structure was evaluated.³⁴ Therefore the entropy of formation of CuFe_2O_4 from CuO and Fe_2O_3 can be estimated as 4.3 ± 0.3 cal deg⁻¹ mole or 18 ± 1.2 J deg⁻¹ mole⁻¹ near 1000°C.

The activities in the spinel solid solution have not been measured in earlier studies. This information is required for deriving the thermodynamic properties of delafossite and cupric ferrite from the oxygen potentials of the three-phase mixtures, $\text{CuO} + \text{CuFeO}_2 + \text{CuFe}_2\text{O}_4(\text{spinel s.s.})$ and $\text{Cu} + \text{CuFeO}_2 + \text{Fe}_3\text{O}_4(\text{spinel s.s.})$ and from the eutectoid decomposition of the spinel solution of equimolar composition near 980°C. The main purpose of this study was to obtain activities in the spinel solid solution by measuring the oxygen potential over mixtures of $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ and Fe_2O_3 at 1000°C. For $x \geq 0.4$ the oxygen pres-

tures are sufficiently high to be measured with a manometer or a McLeod gage in a static system. For $x < 0.4$, an emf method is used to measure the oxygen potential. In separate experiments the composition of the spinel solid solutions in equilibrium with $\text{CuO} + \text{CuFe}_2\text{O}_4$ at 1000°C and $\text{Cu} + \text{CuFe}_2\text{O}_4$ at 900 and 1000°C were measured in order to accurately characterize the phase equilibria. The oxygen potential of the three-phase mixture $\text{Cu} + \text{CuFe}_2\text{O}_4 + \text{Fe}_3\text{O}_4(\text{spinel s.s.})$ was redetermined using a solid oxide galvanic cell. From these results and well established information in the literature, a complete phase diagram was assembled and consistent thermodynamic data for the ternary condensed phases were obtained. From an analysis of the activities in the spinel solid solution information on redox equilibrium represented by Eq. [1] and the distribution of cations and their valencies between the tetrahedral and octahedral sites of the spinel was obtained, which are consistent with the physical measurements cited above.

EXPERIMENTAL

Materials

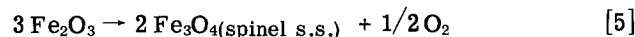
The Cu , Cu_2O , CuO and Fe_2O_3 powders used in this study were obtained from Fisher Scientific Company, while the Fe_3O_4 powder was obtained from Baker Chemical Company. Delafossite (CuFe_2O_4) was synthesized by heating pellets containing an equimolar ratio of Cu_2O and Fe_2O_3 in evacuated silica capsules at 950°C for 48 h. The cupric ferrite (CuFe_2O_4) was prepared by heating pressed pellets containing an equimolar mixture of CuO and Fe_2O_3 for periods up to six weeks at 800°C under a stream of pure oxygen. Cycles of grinding, pelletizing and heating were repeated on each sample to ensure complete reaction. The formation of the compounds was confirmed by X-ray diffraction analysis. The spinel solid solutions were prepared by heating a fine mixture of CuFe_2O_4 and Fe_3O_4 in the required ratio in small evacuated silica capsules for approximately seven days at 1000°C . Since the volume of the capsule was approximately 3 ml, the extent of decomposition of the ferrite solid solution to establish an oxygen pressure in the capsule would be negligible. The capsules were quenched in water after the heat treatment.

Procedure

1. Manometric Measurement of Oxygen Pressure.

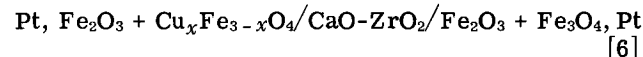
Fine powders of the spinel solid solutions of known composition were mixed with an equal amount of Fe_2O_3 and compacted into pellets. A pellet was placed in a closed-end silica tube connected to a vacuum system and a mercury manometer or McLeod gage. The closed end of the silica tube was held in the constant temperature zone ($\pm 2^\circ\text{C}$) of a Kanthal-world furnace. The hot volume of the silica tube, manometer and the vacuum taps was approximately 100 ml. The silica tube was evacuated by a rotary pump for 15 to 20 min, and the system was then isolated by closing a vacuum tap between the pump and the silica tube. The furnace was heated to 1000°C . The temperature was controlled to $\pm 2^\circ\text{C}$ by a solid state controller. Approximately 3 h after reaching 1000°C , the residual

gases in the silica tube were pumped out for 3 to 10 min depending on composition, and the system was again isolated by manipulating the vacuum tap. The residual pressure in the tube immediately after evacuation was $\sim 10^{-3}$ mm Hg. The pressure gradually increased by the decomposition of Fe_2O_3 according to the reaction,



and attained an equilibrium value in 3 to 6 h. Due to the small volume of the measuring system, the change in the composition of the spinel solid solution resulting from this decomposition is negligible. After measuring the equilibrium pressure, the system was evacuated and partially filled with pure dry oxygen, so that the pressure in the system was approximately twice the equilibrium value. After an incubation period, the pressure was found to drop gradually to the equilibrium value. Longer periods were required to attain equilibrium when approached from higher pressures. A small hysteresis effect (less than 5 pct of the measured pressure) was sometimes observed in the equilibrium values approached from higher and lower pressures. The average of several determinations on each composition is summarized in Table I.

2. Oxygen Potential Measurement with Solid Oxide Galvanic Cells. When the concentration of CuFe_2O_4 in the spinel solid solution was less than 40 mole pct, the oxygen pressure was less than 0.13 mm Hg at 1000°C . An emf cell of this type



was most suited for the oxygen potential measurement under these conditions. The emf of such a cell is directly related to the activity of Fe_3O_4 in the spinel solid solution;

$$\ln a_{\text{Fe}_3\text{O}_4} = -FE/RT \quad [7]$$

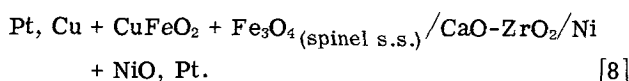
where $F = 23,063 \text{ cal V}^{-1} \text{ mole}^{-1}$, E is the emf in volts, R is the gas constant and T is the absolute temperature. The apparatus and procedure used were identical to that described earlier.³² The emf's (Table II) were reversible and reproducible to ± 1 mv. No attempt was made to measure the temperature coefficient of the emf, since at temperatures significantly below 1000°C some eutectoid decomposition of the spinel solid solution may be expected, and the solubility of Fe_2O_3 in Fe_3O_4 increases significantly with temperature causing some ambiguity in the

Table I. Oxygen Partial Pressures Over the Spinel Solid Solution $\text{CuFe}_2\text{O}_4\text{-Fe}_3\text{O}_4$ in Equilibrium with Hematite at 1000°C Measured with a Manometer or McLeod Gage

Composition of Solid Solution, $X_{\text{Fe}_3\text{O}_4}$	Oxygen Partial Pressure, mm Hg	$a_{\text{Fe}_3\text{O}_4}$, 1000°C	$\gamma_{\text{Fe}_3\text{O}_4}$, 1000°C
0.20	306 ± 1	0.054	0.268
0.40	4.0 ± 0.5	0.159	0.397
0.50	0.56 ± 0.01	0.260	0.519
0.60	0.13 ± 0.01	0.374	0.623

results as a result of the nonstoichiometry of the spinel at temperatures much higher than 1000°C.

The oxygen potential of the three-phase mixture Cu + CuFeO₂ + Fe₃O₄(spinel s.s.) was measured with the cell,



The three-phase electrode was prepared by heating a pellet made from an equimolar mixture of Cu + CuFeO₂ + Fe₃O₄ under purified argon at 1000°C for five days. The emf of the cell showed a linear dependence on temperature,

$$E = 156 + 0.064 T (\pm 2.5) \text{ mv} \quad (850 \text{ to } 1000^\circ\text{C}). \quad [9]$$

3. Composition of the Spinel Solid Solutions in Equilibrium with CuO + CuFeO₂ and Cu + CuFeO₂.

Fine powders of CuO + CuFeO₂ + CuFe₂O₄ and Cu + CuFeO₂ + Fe₃O₄ were mixed in equimolar proportions and compacted into pellets. The pellets were held in evacuated silica capsules and heated at 1000°C for seven days. Preliminary experiments suggested that approximately four days were sufficient to attain equilibrium. A pellet containing Cu + CuFeO₂ + Fe₃O₄ was also equilibrated at 900°C for ten days. At the end of equilibration, the silica capsules were quenched in liquid nitrogen. The pellets were finely ground and the spinel solid solutions were separated magnetically from the other components.

For quantitative wet chemical analysis of the spinel solid solution, copper was separated from iron by precipitation from a 0.4 to 0.5 M hydrochloric acid medium as a sulfide. Total iron in the filtrate was determined by titration with potassium dichromate after reduction with stannous chloride. The copper in the spinel sample was estimated separately by the iodometric and electrodeposition methods. The results are summarized in Table III.

RESULTS AND DISCUSSION

1. Activities in the Spinel Solid Solution

At 1000°C the solubility of Fe₂O₃ in Fe₃O₄ is 3.4 mole pct.³⁵ The oxygen potential corresponding to

Table II. Emf of Cell (6) at 1000°C

Composition of Spinel Solid Solution, X _{Fe₃O₄}	emf, mv	a _{Fe₃O₄} , 1000°C	γ _{Fe₃O₄} , 1000°C
0.70	56.1 ± 1	0.60	0.857
0.80	23.3 ± 1	0.809	1.01

Table III. Composition of the Spinel Solid Solution in Equilibrium with Other Phases of the System Cu-Fe-O

Temperature, °C	3 Phase Equilibria	Composition of Spinel Solid Solution	
		n _{Fe} /n _{Cu} (Molar)	X _{Fe₃O₄}
1000	CuO + CuFeO ₂ + CuFe ₂ O ₄ (spinel s.s.)	2.47	0.135 (±0.01)
1000	Cu + CuFeO ₂ + Fe ₃ O ₄ (spinel s.s.)	26.27	0.89 (±0.02)
900	Cu + CuFeO ₂ + Fe ₃ O ₄ (spinel s.s.)	32.3	0.91 (±0.02)

the Fe₂O₃ + Fe₃O₄ equilibria measured by Charette and Flengas³⁶ can be expressed as,

$$\begin{aligned} \Delta\mu_{\text{O}_2} &= -118,100 + 67.72 T (\pm 150) \text{ cal mole}^{-1} \\ &= -494,100 + 283.34 T (\pm 600) \text{ J mole}^{-1}. \end{aligned} \quad [10]$$

The activity of Fe₃O₄ in the Fe₂O₃ saturated spinel solid solution calculated from the oxygen partial pressures measured in this study using the relation,

$$a_{\text{Fe}_3\text{O}_4} = \left\{ \frac{p_{\text{O}_2}(\text{Fe}_3\text{O}_4 + \text{Fe}_2\text{O}_3)}{p_{\text{O}_2}(\text{spinel s.s.} + \text{Fe}_2\text{O}_3)} \right\}^{1/4} \quad [11]$$

are shown in Table I. The standard state for Fe₃O₄ is the oxygen saturated composition at 1000°C. The variation of the activity of Fe₃O₄ with composition is shown in Fig. 1. The activity of CuFe₂O₄ is calculated by the Gibbs-Duhem relationship,

$$\ln \gamma_{\text{CuFe}_2\text{O}_4} = - \int \frac{X_{\text{CuFe}_2\text{O}_4}}{X_{\text{CuFe}_2\text{O}_4}} = 1 \frac{X_{\text{Fe}_3\text{O}_4}}{X_{\text{CuFe}_2\text{O}_4}} d \ln \gamma_{\text{Fe}_3\text{O}_4} \quad [12]$$

where X is the mole fraction in the spinel solid solution and X_{CuFe₂O₄} is equal to x when the solid solution is represented as Cu_xFe_{3-x}O₄, and γ (= a/X) is the activity coefficient. It can be seen that both components of the solid solution show large negative deviations from Raoult's law.

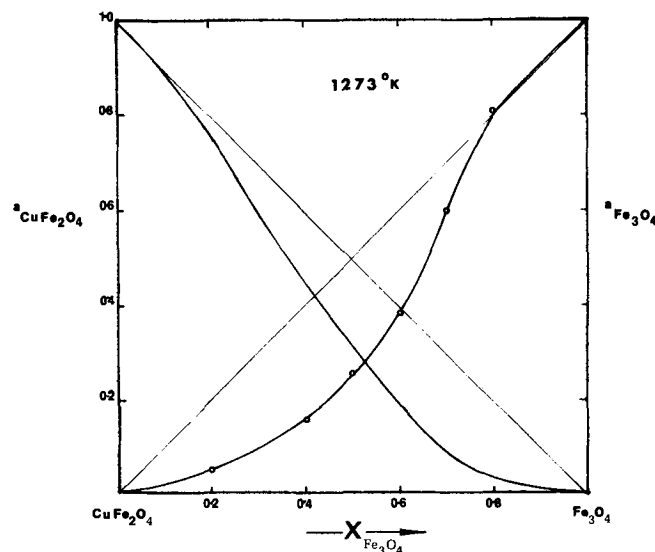
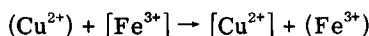


Fig. 1—Activities in the spinel solid solution CuFe₂O₄-Fe₃O₄ at 1000°C.

2. Distribution of Cations and Their Valencies Between the Tetrahedral and Octahedral Sites of the Spinel Lattice

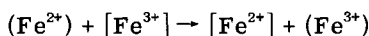
It was shown in an earlier paper³² that the distribution of cations between the tetrahedral and octahedral sites of pure spinels can be estimated from Dunitz and Orgel's³⁷ crystal field octahedral site preference energies, assuming ideal Temkin mixing of cations on each cation sublattice. This treatment can be extended to spinel solid solutions. For NiAl₂O₄-MgAl₂O₄ spinel solid solutions the activities calculated from cation distribution have been found to be in good agreement with values obtained from emf measurements.³⁸

As a first approximation it is assumed that no redox reactions take place between Cu²⁺ and Fe²⁺ ions on the spinel lattice. The competition of the cations, Cu²⁺, Fe²⁺ and Fe³⁺, for the occupancy of the tetrahedral and octahedral sites is governed by site preference energies of the cations. From values tabulated earlier,^{32,37} the following equations are obtained,



$$\Delta G^\circ = -15,200 \text{ cal} = -63,600 \text{ J}$$

$$K = 407.4 = \frac{N_{[\text{Cu}^{2+}]} N_{(\text{Fe}^{3+})}}{N_{(\text{Cu}^{2+})} N_{[\text{Fe}^{3+}]}} \quad [13]$$



$$\Delta G^\circ = -4000 \text{ cal} = -16,740 \text{ J}$$

$$K = 4.86 = \frac{N_{[\text{Fe}^{2+}]} N_{(\text{Fe}^{3+})}}{N_{(\text{Fe}^{2+})} N_{[\text{Fe}^{3+}]}} \quad [14]$$

where () and [] denote the tetrahedral and octahedral sites respectively, and N_i is the ionic fraction of cation i on each site. From definition therefore

$$\sum (N_i) = 1 \quad [15]$$

$$\sum [N_j] = 1. \quad [16]$$

From mass balance,

$$N_{(\text{Cu}^{2+})} + 2N_{[\text{Cu}^{2+}]} = X_{\text{CuFe}_2\text{O}_4} \quad [17]$$

and

$$N_{(\text{Fe}^{2+})} + 2N_{[\text{Fe}^{2+}]} = X_{\text{Fe}_3\text{O}_4} \quad [18]$$

The cation distributions at 1000°C obtained by solving the above equations on a digital computer for different compositions of the spinel solid solution are summarized in Table IV. The ideal cation mixing contri-

bution to the total entropy of the spinel solid solution is given by,

$$\Delta S_{\text{s.s.}}^{\text{CM}} = -R \{ \sum (N_i) \ln (N_i) + 2 \sum [N_j] \ln [N_j] \}. \quad [19]$$

The entropy of mixing of the spinel solid solution is obtained by subtracting from the cation mixing entropy of the solid solution the mole fraction weighted sum of the cation mixing entropy of the two pure component spinels;

$$\Delta S_{\text{s.s.}}^{\text{M}} = \Delta S_{\text{s.s.}}^{\text{CM}} - X_{\text{Fe}_3\text{O}_4} \Delta S_{\text{Fe}_3\text{O}_4}^{\text{CM}} - X_{\text{CuFe}_2\text{O}_4} \Delta S_{\text{CuFe}_2\text{O}_4}^{\text{CM}}. \quad [20]$$

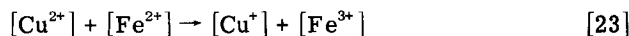
Similarly the heat of mixing of the spinel solid solution due to cation rearrangement can be calculated from octahedral site preference energies;

$$\Delta H_{\text{s.s.}}^{\text{M}} = \left(N_{(\text{Cu}^{2+})_{\text{s.s.}}} - N_{(\text{Cu}^{2+})_{\text{CuFe}_2\text{O}_4} \right) \times X_{\text{CuFe}_2\text{O}_4} 15,200 + \left(N_{(\text{Fe}^{2+})_{\text{s.s.}}} - N_{(\text{Fe}^{2+})_{\text{Fe}_3\text{O}_4} \right) \times X_{\text{Fe}_3\text{O}_4} 4,000 \text{ cal.} \quad [21]$$

The free energy of mixing is given by,

$$\Delta G_{\text{s.s.}}^{\text{M}} = \Delta H_{\text{s.s.}}^{\text{M}} - T \Delta S_{\text{s.s.}}^{\text{M}}. \quad [22]$$

The computed value of $\Delta G_{\text{s.s.}}^{\text{M}}$ is compared with the experimental results in Fig. 2. At the midcomposition of the solid solution the gap between the two sets of values is 1350 cal mole⁻¹ (5,600 J mole⁻¹). The most significant cause of this difference is the reduction of the Cu²⁺ ions by Fe²⁺ ions to give Fe³⁺ and Cu⁺, as suggested by the physical property measurements¹³ cited in the introductory review of literature. To treat this redox reaction quantitatively, the sites of the ions must be specified, since the same ion has different energies on two cation sites. The standard free energy change for the redox reaction, written for the octahedral sublattice,



$$\Delta G_{23}^\circ = -RT \ln K_{23} = -RT \ln \frac{N_{[\text{Cu}^+]} N_{[\text{Fe}^{3+}]}}{N_{[\text{Cu}^{2+}]} N_{[\text{Fe}^{2+}]}}$$

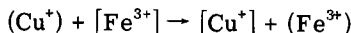
can be computed by fitting the measured free energy of mixing curve. The free energy change for the redox reaction on the tetrahedral site can be simply ob-

Table IV. Calculated Cation Distribution, Entropy, Enthalpy and Free Energy of Mixing of Spinel Solid Solution at 1000°C, Assuming No Reduction of Cu⁺² Ion by Fe⁺² Ion

Composition Spinel Phase, $X_{\text{CuFe}_2\text{O}_4}$	Ionic Fractions, Octahedral Sites			Ionic Fractions, Tetrahedral Sites			$\Delta S_{\text{s.s.}}^{\text{CM}}$ cal deg ⁻¹ mole ⁻¹	$\Delta S_{\text{s.s.}}^{\text{M}}$ cal deg ⁻¹ mole ⁻¹	$\Delta H_{\text{s.s.}}^{\text{M}}$ cal/mol	$\Delta G_{\text{s.s.}}^{\text{M}}$ cal/mol
	$X_{\text{Cu}^{2+}}$	$X_{\text{Fe}^{2+}}$	$X_{\text{Fe}^{3+}}$	$X_{\text{Cu}^{2+}}$	$X_{\text{Fe}^{2+}}$	$X_{\text{Fe}^{3+}}$				
0	0	0.4323	0.5676	0	0.1354	0.8648	3.51	0	0	0
0.2	0.0998	0.3450	0.5552	0.0004	0.1100	0.8896	4.43	1.06	5	-1354
0.4	0.1996	0.2555	0.5449	0.0008	0.0890	0.9102	4.61	1.38	28	-1785
0.6	0.2993	0.1685	0.5322	0.0013	0.0630	0.9357	4.45	1.38	35	-1792
0.8	0.3990	0.0838	0.5172	0.0019	0.0325	0.9667	3.95	1.02	23	-1321
1.0	0.4988	0	0.5012	0.0025	0	0.9975	2.79	0	0	0

tained by subtracting the octahedral site preference energies of the cations involved.

Since the redox reaction introduces another ion, Cu^+ , the distribution of four cations between the two sites must now be considered. The Cu^+ ion has a filled d shell like Zn^{2+} ion and the crystal field theory predicts zero octahedral site preference energy for this electronic configuration. Therefore for the exchange reaction,



$$\Delta G^\circ = 0$$

$$K = 1 = \frac{N_{[\text{Cu}^+]} N_{(\text{Fe}^{3+})}}{N_{(\text{Cu}^+)} N_{[\text{Fe}^{3+}]}} \quad [24]$$

The mass balance equations ([17] and [18]) are also altered by the introduction of Cu^+ ion; the new mass balance being given by,

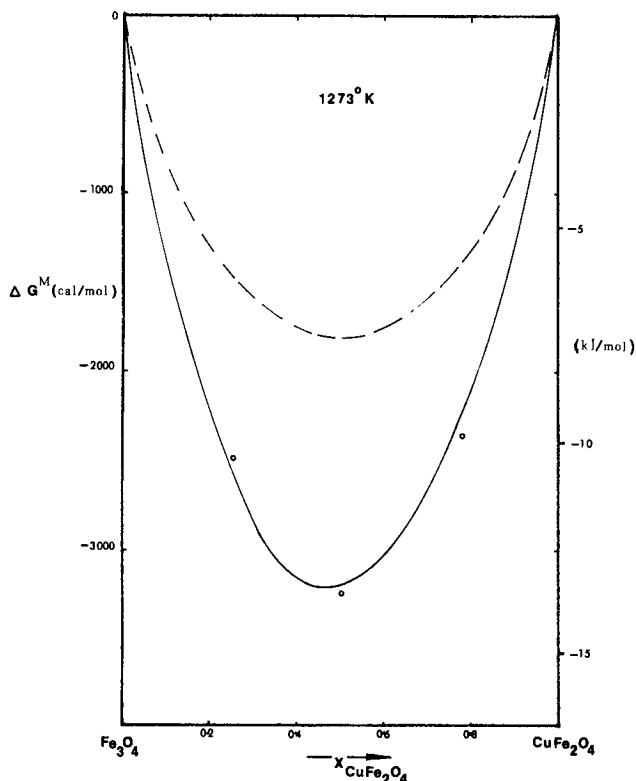


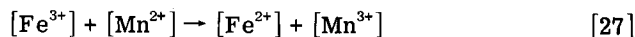
Fig. 2—Free energy of mixing of the spinel solid solution $\text{CuFe}_2\text{O}_4\text{-Fe}_3\text{O}_4$ at 1000°C : — experimental results; - - based on cation distribution model, assuming no reduction of Cu^{2+} ions by Fe^{2+} ions; \circ based on cation distribution model, assuming reduction of Cu^{2+} by Fe^{2+} , $\Delta G_{23}^\circ = -4200$ cal for redox reaction.

$$N_{(\text{Cu}^+)} + 2N_{[\text{Cu}^+]} + N_{(\text{Cu}^{2+})} + 2N_{[\text{Cu}^{2+}]} = X_{\text{CuFe}_2\text{O}_4} \quad [25]$$

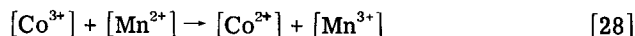
and

$$N_{(\text{Fe}^{3+})} + 2N_{[\text{Fe}^{3+}]} = 2 + N_{(\text{Cu}^+)} + 2N_{[\text{Cu}^+]} \quad [26]$$

The simultaneous Eqs. [13] to [16], [23] to [26] are solved using a digital computer for selected compositions of the spinel solid solution for different values of ΔG_{23}° to obtain the cation distributions. The entropy, enthalpy and free energy of mixing of the solid solution corresponding to each cation distribution is then computed (Eqs. [19] to [22]) and compared with the measured values. The value of ΔG_{23}° for which the calculated and measured free energies of mixing agree is $-4,200$ cal or $-17,600$ J. The corresponding cation distribution is compared in Table V with that suggested by Červinka and Šimša for $X_{\text{CuFe}_2\text{O}_4} = 0.5$. The agreement is satisfactory, considering that Červinka and Šimša arbitrarily assigned all Cu^+ ions to tetrahedral and all Cu^{2+} and Fe^{2+} ions to octahedral sites. This type of assignment, generally followed by physicists, ignores the fact that the exchange of ions between sites never proceeds to completion. The product of distribution ratios being the equilibrium constant for the exchange reaction, there must always be a finite amount of any ion on each of the available sites, although the concentrations may sometimes be negligible. In a subsequent paper, the free energy changes for the redox reactions,



and



will be derived, so that activities in uninvestigated spinel solid solutions containing these species can be predicted with useful accuracy. Since the standard entropy change for redox-exchange reactions are likely to be small, the standard free energy values may be considered to be the same as the standard enthalpy.

3. Phase Equilibria at 1000°C

The Gibbs' triangle representation of phase equilibria in the system Cu-Fe-O based on the results of this study and well established information available in the literature is shown in Fig. 3. From a practical point of view, a more useful representation of phase relations as a function of the oxygen partial pressure (total pressure = 1 atm) at 1000°C is shown in Fig. 4, where the composition coordinate is the ratio of con-

Table V. Cation Distribution, Entropy, Enthalpy and Free Energy of Mixing of Spinel Solid Solution at 1000°C , for a Value of $\Delta G_{(22)}^\circ = -4200$ cal ($-17,600$ J) for the Redox Reaction

Composition Spinel Phase, $X_{\text{CuFe}_2\text{O}_4}$	Ionic Fractions, Octahedral Sites				Ionic Fractions, Tetrahedral Sites				ΔS_{ss}^M cal deg ⁻¹ mole ⁻¹	ΔG_{ss}^M cal deg ⁻¹ mole ⁻¹	ΔH_{ss}^M cal/mol	ΔG_{ss}^M cal/mol
	Cu^{2+}	Cu^+	Fe^{2+}	Fe^{3+}	Cu^{2+}	Cu^+	Fe^{2+}	Fe^{3+}				
0.25	3.0×10^{-2}	5.77×10^{-2}	0.247	0.665	9.5×10^{-5}	7.46×10^{-2}	6.57×10^{-2}	0.8596	4.52	1.19	-950	-2460
0.50	1.10×10^{-1}	8.69×10^{-2}	9.77×10^{-2}	0.707	3.3×10^{-4}	1.06×10^{-1}	2.46×10^{-2}	0.8656	4.59	1.44	-1420	-3250
0.775	0.297	5.17×10^{-2}	1.95×10^{-2}	0.626	1.08×10^{-3}	7.66×10^{-2}	5.95×10^{-3}	0.928	4.12	1.16	-890	-2370
0.50 ¹⁶	1.4×10^{-1}	—	1.05×10^{-1}	0.755	—	2.4×10^{-1}	—	0.76	—	—	—	—

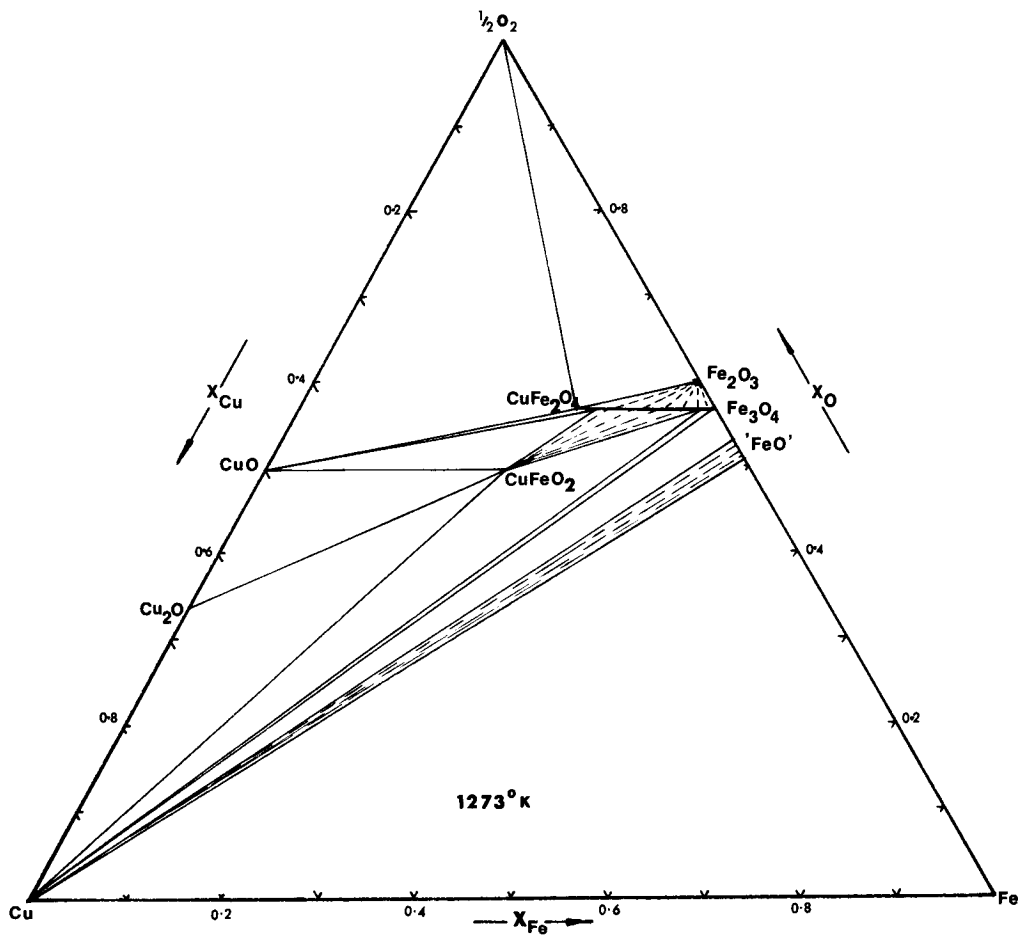


Fig. 3—Gibbs triangle representation of phase relations in the system Cu-Fe-O at 1000°C.

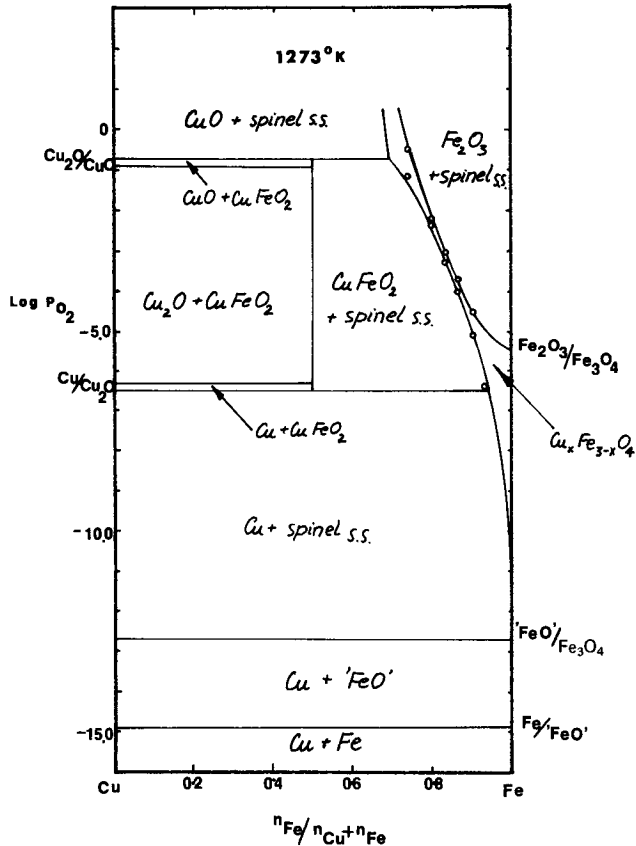


Fig. 4—Phase equilibria in the system Cu-Fe-O as a function of oxygen partial pressure (total press = 1 atm) at 1000°C.

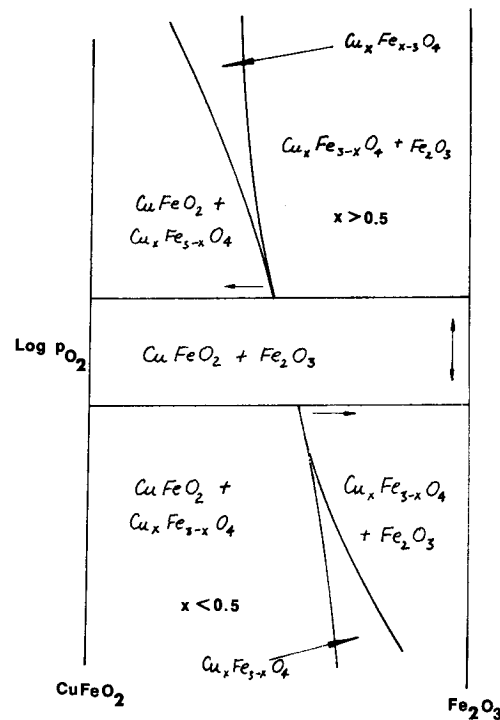


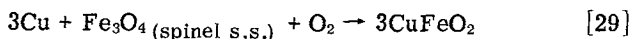
Fig. 5—Schematic representation of the eutectoid decomposition of the spinel solid solution at temperatures below 980°C. The arrows indicate the effect of decreasing temperature.

jugate extensive variable $\eta_{\text{Fe}}/(\eta_{\text{Fe}} + \eta_{\text{Cu}})$. It is seen that the spinel solid solution has a large range of stability, from 1 atm to $10^{-12.7}$ atm oxygen pressure at 1000°C . Another important feature is the narrowness of the spinel phase field in the oxygen partial pressure range $10^{-2.5}$ to 10^{-4} atm, anticipating the eutectoid decomposition of the solid solution in this region at temperatures below 980°C , as shown schematically in Fig. 5. The arrows in the figure indicate the direction in which the composition will change on decreasing the temperature. The oxygen partial pressures and composition of the phases in Fig. 5 at any temperature can be readily calculated, if required, from the quantitative thermodynamic information obtained in this study.

The interesting eutectoid decomposition of the spinel solid solution at temperatures below 980°C into two oxides which are not themselves the constituents of the solid solution can be rationalized on the basis of entropy stabilization of the inverse spinels Fe_3O_4 and CuFe_2O_4 , resulting from mixing of cations. The free energies of formation of these compounds from component oxides becomes more positive with decreasing temperature so that their phases are less stable with respect to other compounds at lower temperature. Other examples of entropy stabilized spinel phases CuAl_2O_4 and Zn_2TiO_4 have been discussed elsewhere.^{34,39}

4. Thermodynamic Properties of Ternary Condensed Phases

The standard free energy of formation of CuFeO_2 can be calculated from the oxygen potential established by the three-phase mixture, Cu, CuFeO_2 and ' Fe_3O_4 ' (spinel s.s.). For the reaction,



the oxygen potential calculated from the emf of cell (8) and the oxygen potential of the Ni + NiO reference electrode⁴⁰ is,

$$\begin{aligned} \Delta\mu_{\text{O}_2} &= -97,520 + 46.48 T (\pm 200) \text{ cal} \\ &= -408,030 + 194.5 T (\pm 830) \text{ J.} \end{aligned} \quad [30]$$

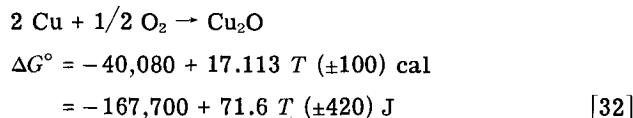
This equation suggests values approximately 600 cal or 2510 J more negative than those obtained by Paulsson *et al.*²⁹ in the temperature range covered in this study.

Zalazinskii *et al.*³⁰ report values for the oxygen potential that are 1200 cal or 5020 J at 1000°C and 2150 cal or 9000 J at 900°C more negative than results obtained in this study.

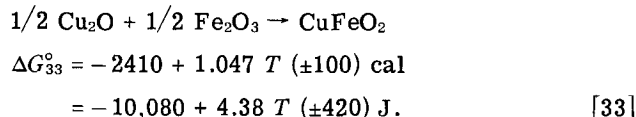
The standard free energy change for Reaction [29] can be computed from the oxygen potential and the composition of the spinel solid solution. Since these compositions lie in region where Raoult's law is obeyed (see Fig. 1),

$$\begin{aligned} \Delta G_{29}^\circ &= \Delta\mu_{\text{O}_2} + RT \ln X_{\text{Fe}_3\text{O}_4} \\ &= -96,880 + 45.74 T (\pm 220) \text{ cal} \\ &= -405,350 + 191.4 T (\pm 850) \text{ J.} \end{aligned} \quad [31]$$

When Eq. [31] is combined with Eq. [10] and the standard free energy of formation of Cu_2O ,⁴¹



one obtains the standard free energy of formation of CuFeO_2 from its component oxides;

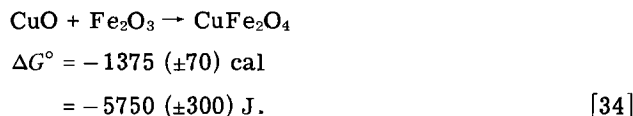


This compares with the equation,

$$\begin{aligned} \Delta G_{33}^\circ &= -5730 + 3.233 T \text{ cal} \\ &= -23,960 + 13.53 T \text{ J} \end{aligned}$$

that may be obtained from values in a recent compilation.⁵ The ratio of heat to entropy of formation of CuFeO_2 from its component oxides obtained in this study is 2302 K, which compares with a value of 2277 K obtained for the formation of CuAlO_2 by an isostructural reaction.³⁴

From the standard free energy of formation of CuFeO_2 , the oxygen potential for Reaction [3] given by Eq. [4], and the activity of CuFe_2O_4 in the solid-solution phase, the standard free energy of formation of CuFe_2O_4 at 1000°C is derived;



When this value for the free energy is combined with the entropy change $4.3 \text{ cal deg}^{-1} \text{ mole}^{-1}$ for Reaction [34] estimated from a semiempirical correlation^{32,33} a value of $+4100 (\pm 500) \text{ cal}$ or $17,150 (\pm 2200) \text{ J}$ for the heat of formation of CuFe_2O_4 at 1000°C is obtained. This value compares with a value of $+5050 (\pm 200) \text{ cal}$ or $21,100 (\pm 840) \text{ J}$ obtained by Navrotsky and Kleppa.³¹ The small discrepancy is probably due to the inhomogeneity of the samples used in the calorimetric experiments. The calorimetric value for the heat of formation in combination with the free energy information obtained in this study suggests that CuFe_2O_4 is unstable below 727°C with respect to a mixture of CuO and Fe_2O_3 . There was evidence during the present study that the spinel can be formed from CuO and Fe_2O_3 at 700°C over a period of several weeks. It therefore appears that the entropy estimated from the semiempirical correlation may be more accurate than that obtained from the free energy values of this study and the calorimetric heat of formation. The following equation is therefore suggested for the free energy of formation of CuFe_2O_4 ;

$$\begin{aligned} \Delta G_{34}^\circ &= 4100 - 4.3 T (\pm 70) \text{ cal} \\ &= 17,150 - 17.99 T (\pm 300) \text{ J.} \end{aligned}$$

The decomposition temperature of CuFe_2O_4 corresponding to this equation is 680°C . The values for activities in the solid solution and free energies of formation of CuFeO_2 and CuFe_2O_4 obtained in this study correctly predict the eutectoid decomposition of $\text{Cu}_{0.5}\text{Fe}_{2.5}\text{O}_4$ at 980°C .

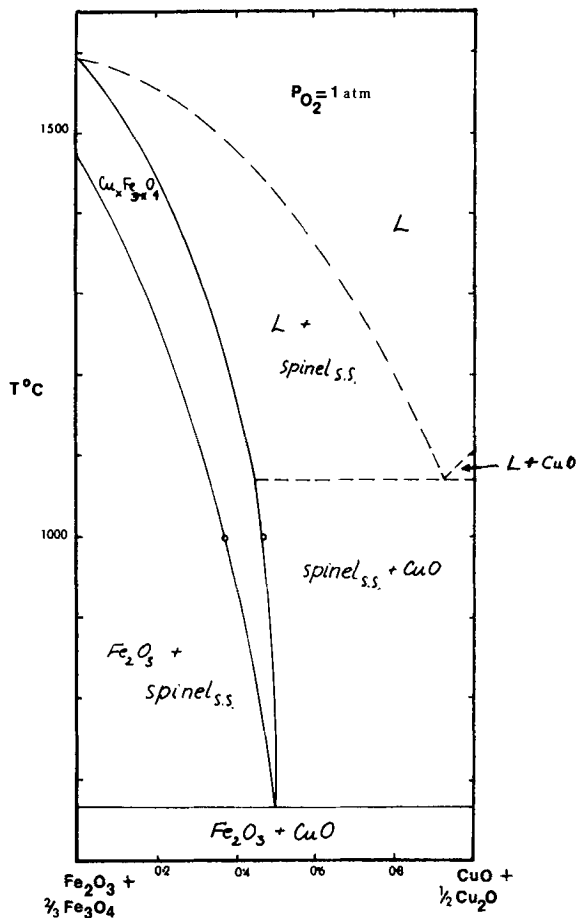


Fig. 6—Isobaric section of the system Cu-Fe-O at 1 atm oxygen pressure.

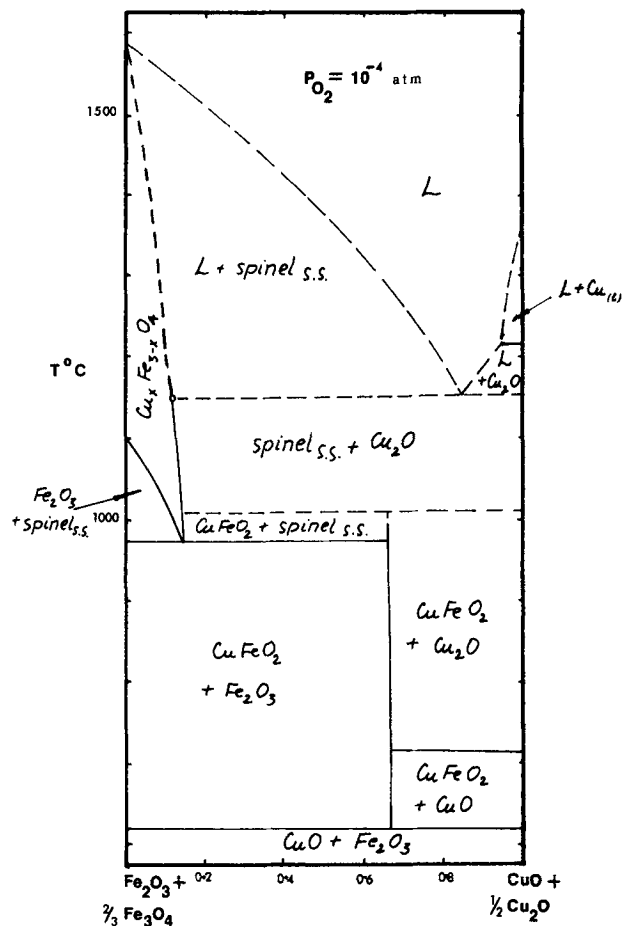


Fig. 7—Isobaric section of the system Cu-Fe-O at 10^{-4} atm oxygen partial pressure.

5. Phase Equilibria as a Function of Temperature at Constant Oxygen Partial Pressures

The values for the heat and entropy of mixing shown in Table V, based on a model of cation mixing in the spinel solid solutions, are used along with other thermodynamic information obtained in this study to calculate the effect of temperature on phase relations at constant oxygen partial pressures. The results for oxygen pressures of 1 and 10^{-4} atm are shown in Figs. 6 and 7. The methods of computation and representation of phase relations are identical to that used earlier for the $\text{Cu}_2\text{O}-\text{CuO}-\alpha\text{Al}_2\text{O}_3$ (Ref. 34) and $\text{Cu}_2\text{O}-\text{CuO}-\beta\text{Ga}_2\text{O}_3$ (Ref. 42) systems. The oxygen potential corresponding to $\text{Cu}_2\text{O}-\text{CuO}$ equilibrium from Ref. 34 and thermodynamic data on the other binary phases like Cu, FeO, Fe_2O_3 , and so forth from Janaf tables⁴³ were used in the calculations. The cuprous ferrite, CuFeO_2 , is unstable at 1 atm oxygen pressure, while both cuprous and cupric ferrite phases are stable at 10^{-4} atm. It is seen from Fig. 6 that at a pressure of oxygen, equal to 1 atm, CuFe_2O_4 phase of stoichiometric composition exists only below 800°C.

Above this temperature, even when excess CuO is present, the ratio $\eta_{\text{Fe}}/\eta_{\text{Cu}} > 2$ in the spinel phase. The deviation resulting from the solubility of Fe_3O_4 in the ferrite increases with decreasing oxygen partial pressure. Since activities in the liquid phase are not

known, and the temperature variation of the activities in the solid solution were not directly measured, some regions of the calculated diagrams indicated by dashed lines must be considered tentative.

SUMMARY

1) The activity of Fe_3O_4 in the $\text{CuFe}_2\text{O}_4-\text{Fe}_3\text{O}_4$ spinel solid solution was obtained from the measurement of the oxygen partial pressure, over the spinel solution in equilibrium with hematite at 1000°C, using emf and manometric techniques. The activities show significant negative deviations from Raoult's law.

2) An analysis of the free energy of mixing of the spinel solid solution on the basis of a cation mixing model suggested considerable reduction of Cu^{2+} ions by Fe^{2+} ions. The free energy of this redox reaction and the distribution of the four cations between the tetrahedral and octahedral sites of the spinel were calculated, and found to be consistent with information from X-ray, magnetic and Seebeck coefficient measurements.

3) The compositions of the spinel solid solutions in equilibrium with $\text{CuO} + \text{CuFeO}_2$ at 1000°C and $\text{Cu} + \text{CuFeO}_2$ at 1000 and 900°C were determined by chemical analysis after magnetic separation of the spinel phases.

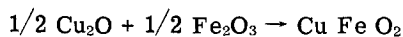
4) The oxygen potential over the three-phase mix-

ture $\text{Cu} + \text{CuFeO}_2 + \text{Fe}_3\text{O}_4(\text{spinel s.s.})$ was measured by a solid oxide galvanic cell, using $\text{Ni} + \text{NiO}$ as the reference electrode.

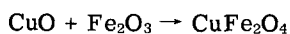
$$\begin{aligned}\Delta\mu_{\text{O}_2} &= -97,520 + 46.48 T (\pm 200) \text{ cal} \\ &= -408,030 + 194.5 T (\pm 830) \text{ J.}\end{aligned}$$

5) From the above measurements and well established information in literature, a complete phase diagram for the system Cu-Fe-O at 1000°C is composed.

6) The standard free energies of formation of CuFeO_2 and CuFe_2O_4 are derived, that are consistent with the phase diagram, oxygen potentials over three phase mixtures, the eutectoid decomposition of $\text{Cu}_{0.5}\text{Fe}_{2.5}\text{O}_4$ below 980°C and other information in the literature. For the reactions,



$$\begin{aligned}\Delta G^\circ &= -2140 + 1.047 T (\pm 100) \text{ cal} \\ &= -10,080 + 4.38 T (\pm 420) \text{ J}\end{aligned}$$



$$\begin{aligned}\Delta G^\circ &= 4100 - 4.3 T (\pm 70) \text{ cal} \\ &= 17,150 - 17.99 T (\pm 300) \text{ J.}\end{aligned}$$

7) The effect of temperature on phase relations in the $\text{Cu}_2\text{O-CuO-Fe}_2\text{O}_3$ system at oxygen pressures of 1 and 10^{-4} atm is graphically illustrated.

ACKNOWLEDGMENTS

The authors are grateful to the National Research Council of Canada for financial support and to Mr. R. H. Chappel for construction of the silica apparatus for manometric measurements.

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