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Thermodynamic Relations among Olivine, Spinel, and Phenacite Structures in Silicates and Germanates. III. The System $CuO–MgO–GeO_2$

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Phase relations in the system $CuO–MgO–GeO_2$ in air at 1000°C were determined. Activity–composition relations in the system CuO–MgO at 1000°C were measured: the guggenite phase was found to exist over the composition range $0.695 < X_{CuO} < 0.805$. The enthalpy and free energy of formation of $CuGeO_3$ were determined by high temperature solution calorimetry and reduction equilibria, respectively. For the reaction: $CuO + GeO_2 = CuGeO_3$, $\Delta G^\circ_{1273} = -4.0$ kcal/mole, $\Delta H^\circ_{988} = -5.2$ kcal/mole, $\Delta S^\circ = -0.9$ cal/deg mole. The stability of rocksalt, tenorite, olivine, enstatite, and $CuGeO_2$ structures in this system is discussed.

1. Introduction

As part of a continuing study of germanate systems (*1*, *2*), this paper reports a determination of phase equilibrium and thermodynamic relationships in the system $CuO–MgO–GeO_2$ This system contains several features of interest. In the binary system CuO–MgO, a phase, guggenite, exists, whose composition, ($CuMgO_2$ (*3*), Cu_2MgO_3 (*4*), or Cu_3MgO_4 (*5*) and structure still remain open to question. The corresponding phase in the system CuO–CoO has been found to have a significant homogeneity range at 1000°C ($0.63 < X_{CuO} < 0.68$) and activity–composition relations have been studied in that system (*6*). In the binary system $CuO–GeO_2$, $CuGeO_3$ is the only compound formed (*7*). This is a "turquoise blue" material, whose structure (*8*) contains chains of almost square planar CuO_4 groups. The nonexistence of the orthogermanate Cu_2GeO_4, or of any compounds in the system $CuO–SiO_2$ (*9*), can be attributed to the energetically unfavorable octahedral coordination of Cu^{2+} in the structures (olivine, spinel, or pyroxene) normally encountered at these compositions in other systems. A study of the ternary system $CuO–MgO–GeO_2$, by determining the extent of copper substitution into the olivine, Mg_2GeO_4 and the pyroxene, $MgGeO_3$ and by making thermodynamic calculations for these solid solutions, would provide a quantitative measure of the instability of $CuGeO_3$ (pyroxene) and Cu_2GeO_4 (olivine).

In the present work, we have carried out three types of experiments. (a) We performed a phase equilibrium study of the system $CuO–MgO–GeO_2$ in air at 1000°C. (b) We determined the equilibrium oxygen pressures needed for the reduction to Cu_2O along the (CuMg)O join and for the reduction of $CuGeO_3$ to Cu_2O and GeO_2. This enabled us to calculate the activity–composition relations in the system CuO–MgO and to compute the free energy of formation of $CuGeO_3$. (c) By calorimetry at 715°C in a molten oxide solvent, we measured the heat of solution of CuO, GeO_2, and $CuGeO_3$ and from that computed the enthalpy of formation of $CuGeO_3$.

2. Experimental

2.1. Phase Equilibrium Studies in Air

The quenching method was used, as described previously (*1*, *2*, *6*). Samples of the desired composition were weighed from dried reagent grade CuO, MgO, and GeO_2, ground

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under acetone, and prereacted in platinum crucibles in a muffle furnace at 1000°C. Small samples of this powder were then held in 30Pd–70Ag capsules, or, when coherent pellets could be pressed, fragments thereof were suspended by thin Pt wire in the hot zone of a vertical Kanthal-wound furnace controlled at 1000 ± 2°C for the equilibration runs. After each run, which lasted 48–72 hr, the samples were air-quenched and the phases identified by X-ray diffraction and/or microscopic observation. Landolt and Muan (*6*) reported the occurrence of quench phases of guggenite in the CuO–CoO system. These formed from solid solutions of rocksalt structure rich in copper. We did not observe any textural differences in any of the guggenite in our samples, and concluded that all the guggenite we saw was at equilibrium at 1000°C. This was borne out by the oxygen pressure measurements in the two phase region (see below). The apparent difference in exsolution kinetics between the CuO–CoO and CuO–MgO systems may be caused by two factors: (a) the more refractory nature of MgO may make all reactions more sluggish than in the CoO-containing system, and (b), the solubility of CuO in the rocksalt phase appears smaller in the MgO-containing system, possibly making the supersaturation during the quench smaller.

The attainment of equilibrium in these runs and in the controlled atmosphere experiments was checked by using several different phase assemblages as starting materials.

2.2. Reduction Studies

2.2.1. System CuO–MgO. The technique used was essentially the same as that of Landolt and Muan (*6*). Nitrogen, purified over copper shot at 250°C, was mixed with compressed air in a conventional gas mixer and the resulting gas mixture was passed upward through the quench furnace. The oxygen pressure for the equilibrium assemblage (CuMg)O, Cu_2O, O_2 was determined in a succession of runs. Small amounts of Cu_2O could readily be detected microscopically in grain-mounts of the powdered sample.

2.2.2. $CuGeO_3$. Since $CuGeO_3$ is the only compound in the system $CuO–GeO_2$, and since no compounds are formed in the system $Cu_2O–GeO_2$ (*7*), it is possible to measure equilibrium oxygen pressures for the phase assemblage ($CuGeO_3$, Cu_2O, GeO_2) by methods analogous to those above. The possible small solubility of Cu_2O in GeO_2 is a complication but the activity of GeO_2 is probably not lowered significantly by this. Speranskaya (*7*) claims a eutectic in the system $Cu_2O–GeO_2$ near 950°C, but her diagram is tentative, and we did not observe any liquid or glassy phase in our reduced samples quenched from 1000°C.

Thus, at 1000°C, we determined the oxygen pressure for the equilibrium phase assemblage ($CuGeO_3$, Cu_2O, GeO_2) by approaching this equilibrium from both sides in a gas-mixer furnace. Because this p_{O_2} was expected to lie in the range 10^{-3}–10^{-4} atm, using air and nitrogen would require very inconvenient mixing ratios (1 : 1000). Accordingly, we calibrated our gas mixer with, and used, purified nitrogen passed over Cu at 250°C and a specially prepared and analyzed tank (Matheson) of nitrogen containing $0.1008 \pm 0.0010\%$ oxygen. In all other respects, these runs did not differ from the (CuMg)O experiments.

2.3. Solution Calorimetry

This technique has been described previously (*10, 11*). The instrument used was a Calvet-type twin microcalorimeter with a Hastelloy block, recently constructed here. Solution experiments, using molten $2PbO–B_2O_3$ at 715 ± 2°C as solvent, were carried out using about 50 mg samples of CuO, GeO_2 (quartz form), and $CuGeO_3$. Platinum calibration pieces were used.

3. Results and Discussion

3.1. Isothermal Section of the System $CuO–MgO–GeO_2$ in Air at 1000°C

This is shown in Fig. 1. Phase relations in the binary system CuO–MgO appear significantly different from those in CuO–CoO. The terminal solubilities in the rocksalt and tenorite phases are much smaller in the magnesium-containing system, and the phase labelled guggenite exists at $0.695 < X_{CuO} < 0.805$, that is, at more copper-rich compositions and over

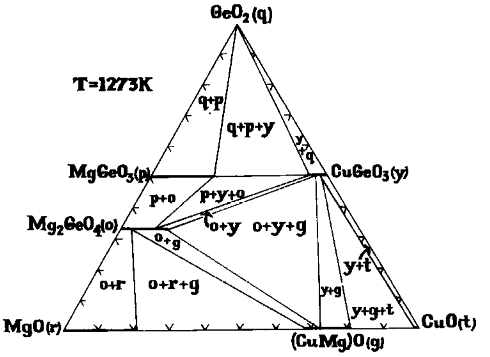

FIG. 1. Isothermal section of the system CuO–MgO–GeO_2 in air at 1000°C.

a somewhat wider homogeneity range than in the cobalt-containing system. This range includes the formula 3CuO·MgO ($X_{CuO} = 0.75$) suggested by Schmahl (*5*), but not the formula 2CuO·MgO ($X_{CuO} = 0.667$) suggested by Driessens (*4*) and others. However, it is not very useful to assign rational formulas to compounds exhibiting a wide range of compositions, and the "compound" Cu_2MgO_3 may well exist at other temperatures. However, the composition CuO·MgO ($X_{CuO} = 0.5$) suggested by Trojer (*3*) clearly falls outside the guggenite range. The composition range $0.812 < X_{CuO} < 0.86$ reported by Ustyantsev *et al.* (*12*) also falls outside our observed guggenite field.

We did not study the structure of the guggenite phase. The lines in our powder X-ray diffraction patterns agreed well with those given by Nitzsche (*13*). No obvious changes occurred in the diffractograms of samples of different compositions. The growth of single crystals of different compositions and structural work on them would be of interest. In view of the wide homogeneity ranges and the different compositions at which the apparently isostructural guggenite phase is found in the two systems CuO–MgO and CuO–CoO, it appears likely that there is some disorder between Cu and Mg or Cu and Co ions on one or more types of sites in the structure. This idea is supported by the observations of Schmahl and Minzl (*5*) that guggenite decomposes to rocksalt plus tenorite phases below about 860°C.

The solubility of CuO in the rocksalt phase was found to be 21% at 1000°C, in good agreement with Schmahl (*5*). This is smaller than the solubility of CuO in CoO (39% (*6*, *14*)) or in NiO (33% (*14*)).

In the ternary system CuO–MgO–GeO_2, the olivine phase accepts up to 20% copper substitution. The solubility of $CuGeO_3$ in the enstatite phase is 36%, and of $MgGeO_3$ in the $CuGeO_3$ phase is 7%. The $CuGeO_3$–$MgGeO_3$ join is pseudobinary. The three phase triangles and two phase quadrilaterals are as shown. None of the two phase regions are large enough to permit the determination of tie lines within them.

3.2. Activity–Composition Relations in CuO–MgO

The results of reduction experiments are shown in Table I. For the reaction

$$(CuO)_{sol} = \tfrac{1}{2}Cu_2O + \tfrac{1}{4}O_2. \qquad (1)$$

$$K = (p_{O_2})^{1/4}(a_{Cu_2O})^{1/2}/a_{CuO}. \qquad (2)$$

Since Cu_2O precipitates as an essentially pure phase one may write:

$$(a_{CuO})_{sol} = (p_{O_2}/p^*_{O_2})^{1/4} \qquad (3)$$

where $p^*_{O_2}$ is the equilibrium oxygen pressure for the reduction of pure CuO. The activity of MgO may then be calculated by Gibbs–

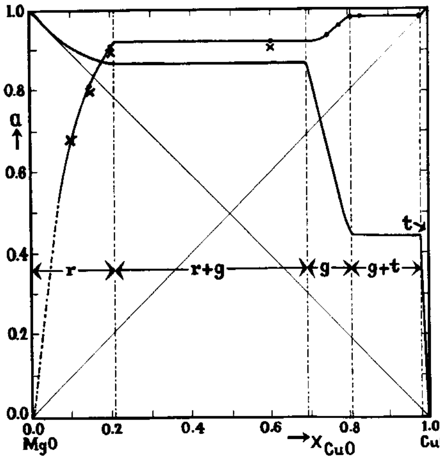

FIG. 2. Activity–composition relations in the system CuO–MgO at 1000°C.

TABLE I

EQUILIBRIUM OXYGEN PRESSURES FOR REDUCTION OF CuO IN SYSTEM $CuO–MgO–GeO_2$ AT 1000°C

Initial composition	Phases[a]	P_{O_2} (atm)[b]	a_{CuO}
CuO	$t+c$	1.28×10^{-1}	1.000
$Cu_{0.98}Mg_{0.02}O$	$t+g+c$	1.20×10^{-1}	0.985
$Cu_{0.83}Mg_{0.07}O$	$t+2+c$	1.20×10^{-1}	0.985
$Cu_{0.78}Mg_{0.22}O$	$g+c$	1.09×10^{-1}	0.960
$Cu_{0.75}Mg_{0.25}O$	$g+c$	9.66×10^{-2}	0.932
$Cu_{0.60}Mg_{0.40}O$	$g+r+c$	9.17×10^{-2}	0.920
$Cu_{0.20}Mg_{0.80}O$	$r+c$	8.78×10^{-2}	0.910
$Cu_{0.15}Mg_{0.85}O$	$r+c$	5.51×10^{-2}..	0.810
$Cu_{0.10}Mg_{0.90}O$	$r+c$	2.74×10^{-2}	0.680
$CuGeO_3 + GeO_2$	$y+q+c$	2.22×10^{-4}	0.200

[a] t = tenorite solid solution; c = cuprite, Cu_2O; g = guggenite solid solution; r = rocksalt solid solution; y = $CuGeO_3$ phase; q = quartz form of GeO_2.

[b] Every p_{O_2} bracketed to approximately ±1% of that value, estimated total error is ±2%.

Duhen integration, and the activity–composition relations are shown in Fig. 2. They agree well with those determined by Schmahl (*5*) for the rocksalt phase and the two-phase region containing rocksalt and guggenite.

The free energy of formation of guggenite from MgO and CuO may then be calculated over its homogeneity range. This is shown in Fig. 3, together with the curve for hypothetical ideal mixing.

The limiting activity coefficients, γ°, of CuO in the rocksalt phase and of MgO in the tenorite phase are 8.00 and 29.2, respectively. We can estimate the free energies of transformation of CuO to the rocksalt structure and of MgO to the tenorite structure from these as:

CuO (tenorite → rocksalt),

$$\Delta G^\circ \sim RT \ln \gamma^\circ_{CuO} = 5.3 \text{ kcal/mole} \quad (4)$$

and

MgO (rocksalt → tenorite),

$$\Delta G^\circ \sim RT \ln \gamma^\circ_{MgO} = 8.5 \text{ kcal/mole.} \quad (5)$$

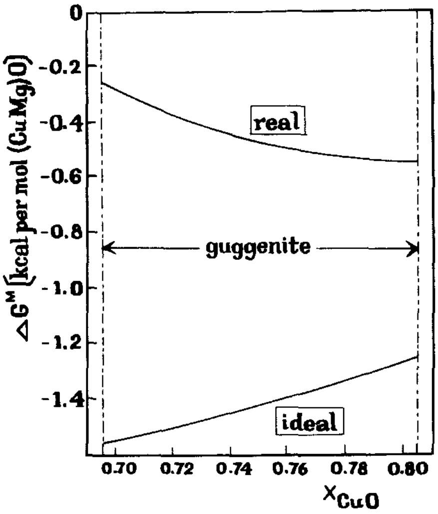

FIG. 3. Free energy of formation of guggenite from CuO and MgO at 1000°C.

For the CuO transformation, Schmahl (*15*) quotes a value of 2.3 kcal/mole, but does not present the data to substantiate it. From his earlier paper (*5*), however, in which activity–composition relations in CuO–MgO are presented, and are very similar to those given here, a value of the free energy of transformation very similar to our 5.3 kcal can be calculated. On the basis of calorimetric studies, Navrotsky and Kleppa (*16*) have suggested that ΔH^0 for the transformation should be in the range of 4–5 kcal. Since ΔS^0 for such a solid state transition is probably not more than 1.5 cal/deg mole in magnitude, a ΔG°_{1273} value of 5.3 kcal is very reasonable. Landolt and Muan (*6*), on the other hand, estimate $\Delta G^\circ_{1273} = 2.3$ kcal from activity–composition relations in the system CuO–CoO, where the extent of the rocksalt phase is much greater than in CuO–MgO. One must caution, that, in the CuO–MgO system, the very distinct curvature of the a_{CuO} curve in the rocksalt phase precludes a really accurate determination of the limiting Henry's Law slope, so that the discrepancies between these various studies may be caused by such uncertainties.

The approximate value of ΔG° for the relation MgO (rocksalt → tenorite) is similar to that for the same hypothetical transformation in CoO (*6*).

3.3. *Enthalpy and Free Energy of Formation of $CuGeO_3$ from the Oxides*

From the reduction studies presented in Table I, we have

$$CuO \rightarrow \tfrac{1}{2}Cu_2O + \tfrac{1}{4}O_2, \; p^*_{O_2} = 0.128 \text{ atm} \qquad (6)$$

and

$$CuGeO_3 = \tfrac{1}{2}Cu_2O + GeO_2 + \tfrac{1}{4}O_2, \quad p_{O_2} = 2.22 \times 10^{-4} \text{ atm.} \qquad (7)$$

Then for the reaction

$$CuO + GeO_2 = CuGeO_3, \quad K = (p^*_{O_2}/p_{O_2})^{1/4} = 4.90 \qquad (8)$$

and $\Delta G^\circ = -RT \ln K = -4.0$ kcal.

The calorimetric data are presented in Table II. The enthalpy of Reaction (8) is equal to the difference in the heats of solution of

$CuO + GeO_2$ and of $CuGeO_3$

$$\Delta H_f{}^\circ = \Delta H_{\text{sol}(CuO)} + \Delta H_{\text{sol}(GeO_2)} - - \Delta H_{\text{sol}(CuGeO_3)} = -5.2 \pm 0.4 \text{ kcal/mole.} \qquad (9)$$

Then, the standard entropy of formation of $CuGeO_3$ from the oxides is:

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T = -0.9 \text{ cal/deg mole.} \qquad (10)$$

The fairly substantial negative heat and free energy of formation of $CuGeO_3$ is consistent with Speranskaya's phase diagram for the system CuO–GeO_2 (*7*), which shows $CuGeO_3$ to melt congruently in air some 50° above the temperature at which CuO is reduced to Cu_2O. The small negative entropy change is characteristic of solid state reactions with no substitutional disorder in reactants or products.

The negative enthalpy of formation of $CuGeO_3$ is to be contrasted with positive enthalpies of formation for the spinels $CuFe_2O_4$ (*16*), $CuGa_2O_4$ (*16*), $CuMn_2O_4$ (*16*), and $CuCr_2O_4$ (*17*). These compounds are "entropy-stabilized" by octahedral–tetrahedral site cation disorder, while the copper silicates, titanates, and orthogermanate do not exist. We have previously attributed these

TABLE II

HEATS OF SOLUTION OF CuO, GeO_2, AND $CuGeO_3$ IN MOLTEN $2PbO \cdot B_2O_3$ AT 713 ± 1°C

(mg) Sample	$\Delta H^m{}_{\text{sol}}$ (kcal/mole)
CuO (tenorite)	
51.51	8.388
103.81	8.480
78.20	8.870
96.03	8.130
53.00	8.968
85.98	8.696
75.75	8.655
74.71	8.458
84.16	8.323
64.04	8.261
	av = 8.52 ± 0.27 (10)[a]
GeO_2 (quartz)	
81.87	−4.877
114.58	−5.031
83.66	−5.025
84.35	−5.143
79.00	−5.027
69.36	−4.615
86.30	−4.976
	av = −4.96 ± 0.17 (7)
$CuGeO_3$	
71.12	8.516
80.53	8.785
96.02	8.558
100.80	9.013
82.17	8.482
84.94	8.565
68.62	9.101
98.82	8.960
66.12	9.108
56.86	8.807
	av = 8.82 ± 0.22 (10)

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[a] Error given is standard deviation, number in parentheses is number of experiments performed.

unfavorable energetics of copper spinel formation to the forced change in copper coordination from square planar in tenorite to octahedral and partly tetrahedral in the spinels ~~(16)~~. The negative heat of formation of $CuGeO_3$, in which the copper ion retains a coordination similar to that in tenorite, further supports this view.

3.4. Discussion: Stability of Ternary Solid Solutions and Structural Transformations

As seen from Fig. 1, none of the two-phase fields (rocksalt plus olivine, guggenite plus olivine, guggenite plus $CuGeO_3$, tenorite + $CuGeO_3$, olivine + pyroxene, olivine + $CuGeO_3$, guggenite + $CuGeO_3$, rocksalt + $CuGeO_3$) are very extensive. We felt this diagram was thus too complex to apply the method developed by Muan (*18*) to calculate activity–composition relations along the $(CuMg)_2GeO_4$ and $(CuMg)GeO_3$ joins from the direction of conjugation lines. However, some very approximate calculations can be made as follows. The $MgGeO_3$–$CuGeO_3$ join is pseudobinary, the limits of the enstatite and $CuGeO_3$ phases occur at $X_{CuGeO_3} = 0.36$ and 0.93, respectively. If one takes, as an admittedly crude approximation, that the solute follows Henry's Law and the solvent follows Raoult's Law throughout each single phase region, then the activity coefficient of $CuGeO_3$ in the enstatite phase is $\gamma_{CuGeO_3} = a_{CuGeO_3}/X_{CuGeO_3} = 0.93/0.36 = 2.58$, while the activity coefficient of $MgGeO_3$ in the $CuGeO_3$ phase is $\gamma_{MgGeO_3} = a_{MgGeO_3}/X_{MgGeO_3} = 0.64/0.07 = 9.14$.

Then for the transformation

$CuGeO_3(CuGeO_3 \rightarrow \text{enstatite})$,

$$\Delta G^\circ = RT \ln \gamma_{CuGeO_3} = +2.4 \text{ kcal/mole} \qquad (11)$$

and for

$MgGeO_3 (\text{enstatite} \rightarrow CuGeO_3)$,

$$\Delta G^\circ = RT \ln \gamma_{MgGeO_3} = +5.6 \text{ kcal/mole}. \qquad (12)$$

Both these values are fairly similar to those for the transformations between structures having corresponding coordination in the binary oxides CuO and MgO (see Section 3.2).

The substitution of copper into the olivine phase is quite limited; olivine becomes unstable relative to $(CuMg)GeO_3$ and guggenite at $X_{Cu_2GeO_4} = 0.20$. This suggests that Cu_2GeO_4 olivine is unstable with respect to disproportionation into $CuGeO_3$ and CuO by several (3–5) kcal, which would make its free energy of formation from the oxides zero or slightly positive. A similar conclusion has been reached previously (*11*) about its heat of formation.

We also performed a few hydrothermal experiments at 730°C and 0.5 kbar water pressure to determine the extent of the $(CuMg)_2GeO_4$ spinel solid solution, since under those conditions Mg_2GeO_4 has the spinel structure. Preliminary results indicate single phase spinels form for $X_{Cu_2GeO_4} < \sim 0.2$. Though no quantitative interpretation can be made, these data suggest that the spinel form of Cu_2GeO_4 would be of fairly comparable stability (or instability) to the olivine.

Acknowledgments

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