analysis of the latter data suggests that a theory which assumes repulsive forces between non-bonded adjacent atoms is much more consistent with experiments than a theory assuming attraction. However neither theory is capable, in a simple formulation, of accounting quantitatively for the observed changes in the heats of addition reactions.

Mallinckrodt Chemical Laboratory
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[Contribution from the Department of Chemistry, the Rice Institute]

X-Ray Diffraction Studies in the System $CuO–Fe_2O_3$

By W. O. Milligan and James Holmes

Cupric ferrite, $CuFe_2O_4$, has been synthesized by Holgersson[1] and by Wartmann and Thompson.[2] These investigators found it necessary to heat mixtures of cupric and ferric oxides to high temperatures, around 1000°. More recently Forestier and Longuet[3] reported that the gel prepared by adding sodium hydroxide to a mixture of cupric and ferric salts, and boiling for several hours, gave an X-ray diffraction pattern corresponding to cupric ferrite. Since this observation is inconsistent with the earlier work at high temperatures, and with the usual behavior of hydrous oxides upon aging,[4] further studies were made on this system. This paper reports the results of a systematic X-ray study of mixtures of varying composition of cupric and ferric oxides, precipitated at 25°, aged under water at 100°, and heated to 1000°.

Experimental

Preparation of Samples.—A slight excess of sodium hydroxide was added dropwise to rapidly stirred mixtures of freshly prepared cupric and ferric chloride solutions[5] at 25°. The compositions of the chloride solutions were adjusted so that there was obtained a series of oxides containing 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mole per cent. (anhydrous basis) of cupric oxide. The precipitated gels were washed with distilled water, using a centrifuge, until the supernatant liquid was free of chloride ions, and air-dried at room temperature.

Portions of the air-dried samples were suspended in water at 100° for a period of twenty-four hours in a flask fitted with a reflux condenser, and air-dried at room temperature.

A second portion of each air-dried sample was heated for an hour at 1000° in a muffle furnace, quenched in cold water, and air-dried. A duplicate series of samples was prepared from nitrate solutions according to the directions of Wartmann and Thompson[2] and heated to 1000°.

X-Ray Analysis.—X-Ray diffraction patterns were obtained for the samples described above, using Mo K_α X-radiation. The results obtained for the original air-dried samples (Fig. 1), the samples aged at 100° (Fig. 2), and the samples heated to 1000° (Fig. 3) are given in the form of charts. The X-radiograms obtained for the samples prepared from the nitrate solutions are identical with those given in Fig. 3.

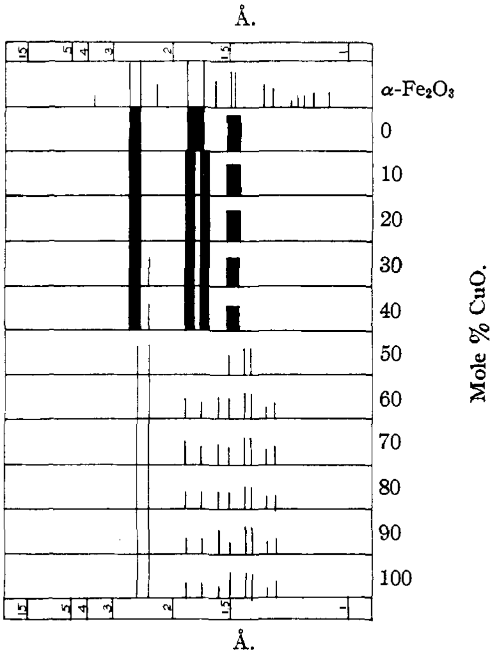

Fig. 1.—X-Ray diffraction diagrams for cupric and ferric oxides precipitated at 25°.

Discussion

It is concluded from the X-radiograms of the original air-dried samples (Fig. 1) that there is no indication of the formation of cupric ferrite at 25°. The samples consist of mixtures of ferric oxide and cupric oxide. The pattern from the pure ferric oxide consists of a few broad bands, in

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[1] Holgersson, *Chem. Zentr.*, **100**, I, 372 (1929).

[2] Wartmann and Thompson, Bur. Mines, Dept. Investigations, No. 3228, p. 15 (1934).

[3] Forestier and Longuet, *Compt. rend.*, **208**, 1729 (1939).

[4] Weiser and Milligan, *Chem. Rev.*, **25**, 1 (1939); Weiser, "Inorganic Colloid Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1935.

[5] Old ferric chloride solutions may contain colloidal β-$Fe_2O_3 \cdot H_2O$: *cf.* Weiser and Milligan, This Journal, **57**, 238 (1935).

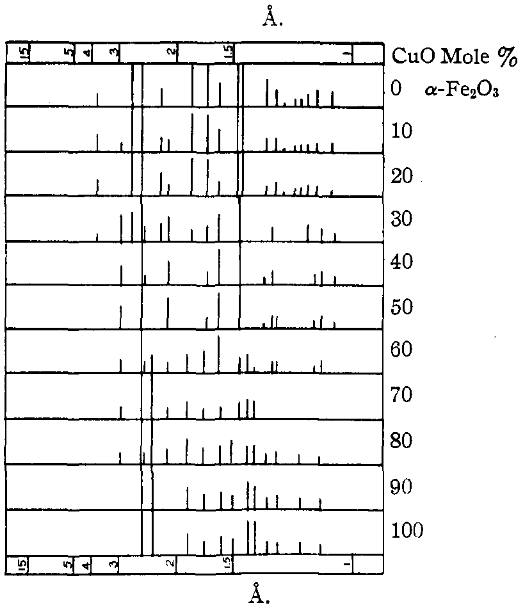

Fig. 2.—X-Ray diffraction diagrams for cupric and ferric oxides heated to 1000°.

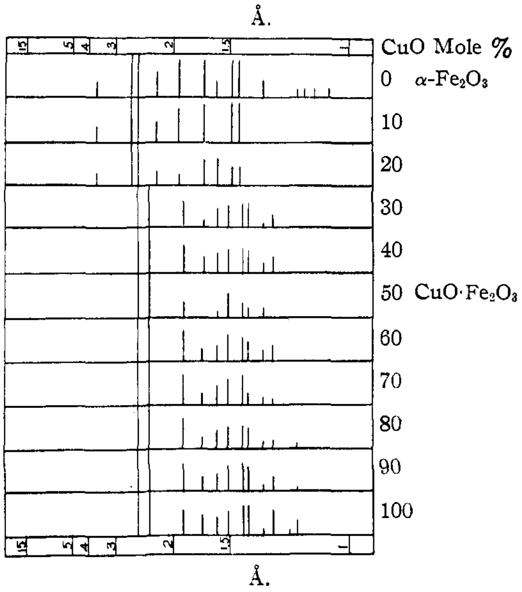

Fig. 3.—X-Ray diffraction diagrams for cupric and ferric oxides aged at 100°.

agreement with earlier results obtained for the freshly precipitated oxide.[6] At a composition of about 10 mole per cent. cupric oxide, one would hardly expect to detect the pattern of cupric oxide, but since the pattern for this oxide is not obtained at 10 to 30 mole per cent., it follows that the ferric oxide is inhibiting the crystallization of the copper oxide. It should be observed that there is no indication of the formation of cupric hydroxide.

The results for the samples aged at 100° are very similar. The sharp pattern of α-Fe_2O_3 obtained for the pure ferric oxide confirms previous results from this Laboratory.[6] At compositions of 10 to 30 mole per cent., where the amount of cupric oxide is sufficient to be detected if it were crystalline to X-rays, only a relatively sharp α-Fe_2O_3 pattern is obtained. This shows that the ferric oxide is still inhibiting the crystallization of the cupric oxide. At relatively high concentrations of cupric oxide only the pattern of this oxide can be detected, demonstrating that in this region the crystallization of the ferric oxide is being inhibited. At intermediate compositions the patterns of both ferric and cupric oxides are obtained. There is no indication of the formation of cupric ferrite in the samples aged at 100°, in agreement with the observations of Wartmann and Thompson, but in contrast to the results reported by Forestier and Longuet.

The samples heated for an hour at 1000° are all crystalline. The formation of the cubic cupric ferrite is clearly shown at 50 mole per cent. The X-radiograms of samples containing 40 or 60 mole per cent. of cupric oxide correspond to a mixture of cupric ferrite and α-Fe_2O_3 or CuO, respectively. There is no indication of solid solution, or of the formation of more than one cupric ferrite. The observed lattice constant agrees so closely with the values of Holgersson and of Wartmann and Thompson, that the observed interplanar spacings are not tabulated in this paper.

Summary

The following is a brief summary of the results of this investigation:

1. X-Radiograms of mixtures of cupric and ferric oxides precipitated together at 25° show no indication of the formation of cupric ferrite.
2. The results are similar for samples aged by boiling under water for twenty-four hours, except that sharper X-ray diffraction patterns of α-ferric oxide and cupric oxide are obtained. These observations are in agreement with the results of Wartmann and Thompson and with Holgersson, but are in contrast to the results of Forestier and Longuet.
3. It is concluded from X-ray diffraction patterns of the samples heated to 1000°, that $CuFe_2O_4$ is the only compound formed in the system CuO–Fe_2O_3.

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[6] Weiser and Milligan, *J. Phys. Chem.*, **39**, 25 (1935); *cf. ibid.*, in press.