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## The Cuprous-Cupric Complex in Hydrochloric Acid Solution

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## The Cuprous-Cupric Complex in Hydrochloric Acid Solution

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In the process described by Diehl and Brouns (1) for the direct determination of copper in bronze by electrodeposition from hydrochloric acid solution using hydroxylammonium chloride as anodic depolarizer and controlling the cathode potential automatically (3), the sample of bronze is dissolved in hydrochloric acid by the dropwise addition of nitric acid or of hydrogen peroxide. Subsequently the solution is diluted and electrolyzed, the cathode reaction being first the reduction of cupric ion to the chlorocuprous ion,  $\text{CuCl}_2^-$ , and then the deposition of copper. The time of electrolysis can be materially shortened if the first reduction is effected chemically, by the addition of hydroxylammonium chloride or of stannous chloride. If the reducing agent be added to the solution before it is diluted, that is, to a fairly concentrated hydrochloric acid solution, the solution turns dark brown or black, the color being due to some material in solution which disappears on dilution. It became of interest to learn more of this dark colored solution, particularly since it was observed that a small amount of antimony did or did not deposit with the copper depending on whether the reduction was made before or after the dilution.

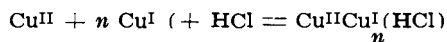
Quite evidently this dark brown solution is a complex ion containing both cupric and cuprous copper and undoubtedly also a considerable amount of hydrochloric acid. A library search uncovered old work by Poma on this very subject. Poma found (4) that the solubility of cuprous chloride in hydrochloric acid solutions increased in the presence of dissolved cupric chloride indicating the formation of a cuprous-cupric complex. In a later paper (5) Poma measured the electrical conductance of hydrochloric acid solutions containing cuprous and cupric copper. He measured also the potentials of such solutions toward a platinum electrode but was unable to draw a conclusion as to the nature of the complex. However, a migration experiment clearly indicated that the complex carried a negative charge. A few years later Sandonnini (6), in the course of an extensive investigation of binary salt mixtures, made a thermal analysis of the cuprous chloride-cupric chloride system. Although mixtures containing more than 40 per cent cupric chloride lost chlorine rapidly the results indicated the presence of a salt having the composition  $2\text{CuCl} \cdot \text{CuCl}_2$  corresponding to 40.5 per cent cuprous chloride and 59.5 per cent cupric chloride.

Other cases of compound formation in melts of binary salt mixtures were found by Sandonnini; to have such a double salt persist on passage into solution, however, is remarkable. While it might be

<sup>2</sup>This work was carried out as a senior research project.

supposed that the compound in solution is the same as that found in the fused mixture, there is no direct evidence in proof of this, the Poma work being qualitative or at least not interpreted so as to establish the composition of the compound.

In the work to be described, the ratio of cuprous copper to cupric copper in the complex in solution has been determined by the method of continuous variations. Assuming the reaction to be of the form



the problem is to determine the value of  $n$ . The method of continuous variations, originally devised by Job (3) and recently reviewed and applied to a number of problems by Vosburg (7), is a mathematical process for determining the number of molecules of one substance combining with another to yield a new compound, given the values for different mixtures of some physical property which differentiates the complex from the reactants. In this case spectrophotometric measurements at various wave lengths were made on mixtures of cupric and cuprous copper in concentrated hydrochloric acid solutions. The total concentration of copper was held constant at 0.05 M and the relative amounts of cupric,  $(0.05-x)$ , and cuprous copper  $x$ , were varied. The concentration of hydrochloric acid was held constant at 11.2 M (concentrated hydrochloric acid) and the transmittancy measured over the visible spectrum. From the optical density of the various solutions so observed is subtracted the calculated density the solution would have had had no reaction occurred. This difference, when plotted as a function of  $x$ , has a maximum or minimum value such that

$$n = \frac{x}{0.05-x}$$

The results indicated that the complex contains one atom of cuprous and one atom of cupric copper. Thus, the material in solution does not correspond to the two to one compound found by Sandonini in the solid state. In this soluble compound there is undoubtedly bound a considerable amount of hydrochloric acid but nothing can be said from the present work as to the number of chloride radicals entering the complex. A migration experiment carried out here confirmed that of Poma, indicating that the complex carries a negative charge.

#### EXPERIMENTAL WORK

**Standard Solutions.** Owing to the extremely rapid oxidation of the chlorocuprous ion by oxygen elaborate precautions were exercised to avoid the admission of air during the preparation and measurement of the solutions. The stock solutions of cupric chloride in hydrochloric acid were stored in Machlett burets. A stream of nitrogen, freed of oxygen by passage through alkaline pyrogallol

and saturated with hydrogen chloride by passage through concentrated hydrochloric acid, was passed through the storage bulbs of each buret.

The solution of the chlorocuprous ion was prepared by dissolving Mallinkrodt, c.p. cuprous chloride in hydrochloric acid. Copper wire was placed in the bulb of the buret and sufficient time allowed for any cupric ion to be reduced as evidenced by the decolorization of the solution



The copper in this solution was determined electrolytically by the method of Diehl and Brouns (1, 2); found, 0.984 M.

The solution of cupric copper was prepared by dissolving c.p. cupric chloride in concentrated hydrochloric acid. It also was standardized electrolytically; found: 0.778 M.

Both solutions were restandardized at intervals during the work and the latest values used in calculating the amounts of solution taken in preparing the various mixtures.

**Apparatus.** In order to avoid oxidation of the cuprous copper and apparatus was devised by which the mixing and measurement could be carried out without exposure to air, Figure 1.

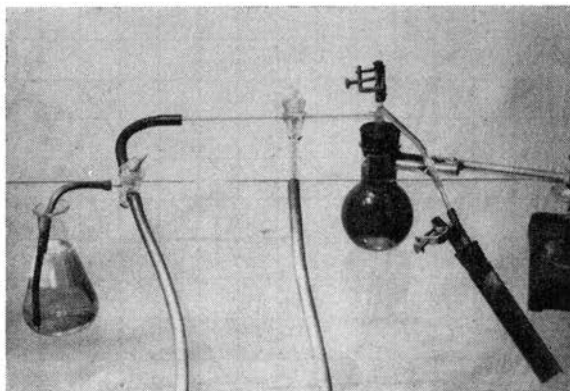


Figure 1. Apparatus for mixing and filling cuvette with cupric chloride, cuprous chloride, and hydrochloric acid solutions without contact with air.

The entire system was evacuated through the stopcock and tube at the center, the pressure being indicated on a manometer (not shown) in the vacuum line. Nitrogen was then admitted to the system through the tube at the left until the manometer indicated at atmospheric pressure. The vacuum line was then shut off ahead of the manometer and nitrogen was then admitted to the system through the tube at the left until the manometer indicated atmospheric pressure. The system was again evacuated and nitrogen again

introduced. The vacuum tube was disconnected, the three way stopcock opened at all three lines, and the nitrogen pressure adjusted to give a continuous flow of gas through the open arm of the cock. The screw clamp on the mixing chamber was opened allowing nitrogen to escape from it also and the tip of the Machlett buret inserted through the tube. The requisite amounts of cuprous and cupric solutions and of oxygen free hydrochloric acid were thus introduced and mixed by shaking. The mixture was then forced by gentle nitrogen pressure into the cuvette, shown at the right, which was then disconnected, closed off and inserted in the spectrophotometer.

**Spectrophotometric Measurements.** A Coleman Double Monochromator was employed for the measurements. A slit width of  $30\text{ }\mu$  was used. Round, clear glass cuvettes, 1.5 cm. internal diameter were used. The total copper concentration was held constant at 0.05 M and the ratio of cuprous copper,  $x$ , to cupric copper,  $(0.05x)$ , varied in steps at intervals of 0.005 M. The spectral distribution curves are given in Figure 2 for the pure cuprous solution, the pure cupric solution and for the solution 0.025 M in both cuprous and cupric copper, the mixture at which the concentration of the complex is near its maximum.

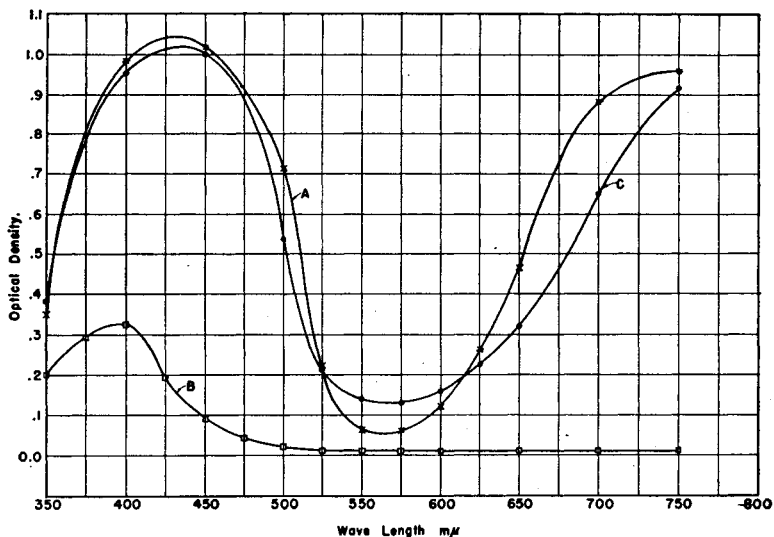
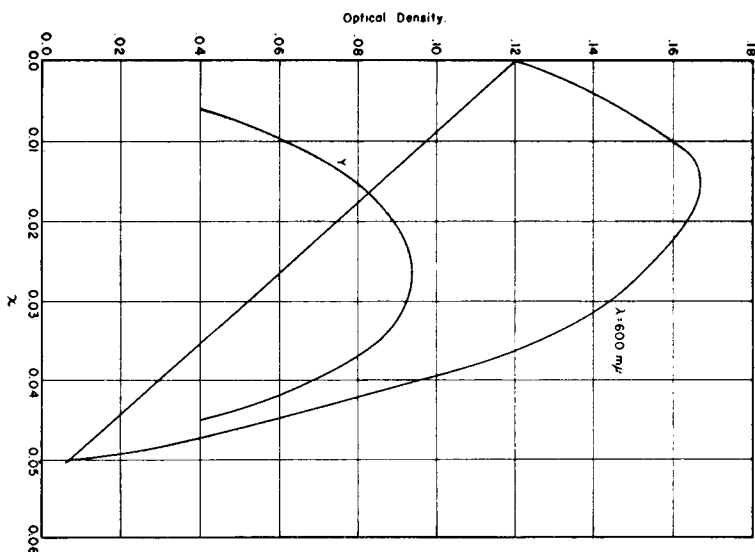
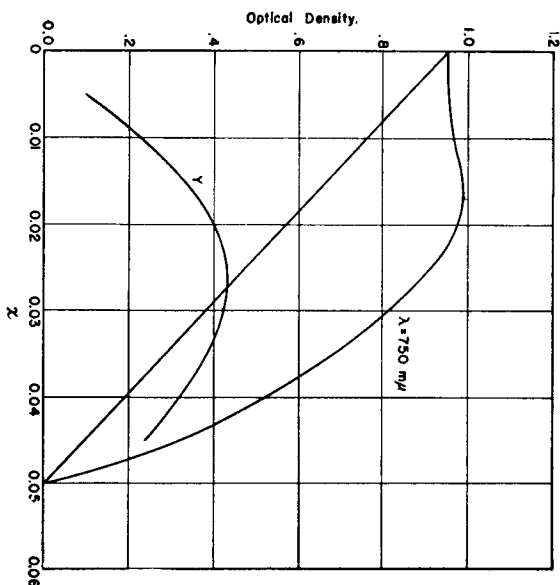


Figure 2. Absorption spectra of 0.05 M cupric chloride, A, 0.05 M cuprous chloride, B, and 0.025 M cupric chloride plus 0.025 M cuprous chloride, C; all in 11.2 M hydrochloric acid.

The absorption of the cuprous chloride solution above  $500\text{ m}\mu$  is so low that it makes practically no contribution, the solution appearing to the eye to be practically colorless. The cupric chloride solution is green corresponding to the absorption minimum near

560  $m\mu$ . The cuprous-cupric mixture absorbs more of the green, but considerably less of the red and somewhat less of yellow and blue, accounting for its brown hue.

The absorption of the eleven solutions, (pure cupric, pure cuprous and nine mixtures) was determined as a number of wave lengths. The absorption for two such series of measurements, at 600  $m\mu$  and at 750  $m\mu$  are given in Figures 3 and 4.



Figures 3, 4. Absorption of hydrochloric acid solutions 0.05 M in

total couper,  $x$  M in cuprous chloride and  $(0.05-x)$  M in cupric chloride. The straight line is the optical density assuming no reaction to occur. The curve Y is the difference between the density curve and the straight line.

The straight line connects the optical density values of the two pure solutions and from it was obtained the density the mixture would have had had no reaction occurred. The third curve is the difference between the observed absorption and the calculated absorption on the assumption of no reaction.

In Figures 3 and 4 it is seen that a maximum occurs at  $\omega = 0.5$ , from which  $n$  is seen to have the value of one. At all of the wave lengths examined, 525, 550, 600, 625, 650, 700 and 750 m, the maximum occurred at  $x = 0.5$ . The cuprous-cupric complex thus appears to be on to one compound,  $\text{CuCl}_2 \bullet \text{CuCl}$ .

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