copper 49.1%, equaling 78.7%. If water of combination be considered as making up the balance, these values are in close agreement with the formula $CuN_3.2H_2O$.

From a sample representing 0.0348 g. material was obtained 0.0368 g. AgN_3, equivalent to 0.0103 g. N_3 (= 29.6%). This weight of nitrogen, on the basis of the formula $CuN_3.2H_2O$, is equivalent to 0.0156 g. copper, (found, 0.0167 g. copper) and to 0.0088 g. water; total, 0.0347 g.

Under the conditions existing in these experiments, one would expect to obtain cuprous trinitride. In the absence of a determination of water, it cannot be said with definiteness whether the formula proposed represents the actual composition of the compound, or is in agreement with the values obtained only through a coincidence.

The excess in copper over nitrogen, it may be pointed out, is to be expected when it is remembered that a reaction between a solid and a liquid may quite easily be incomplete, due to the protective coating on the solid of the product of the reaction, where the product is likewise a solid. It is to be expected, then, that a small amount of cuprous oxide would still be present.

The application of the results described in the foregoing paragraphs to the anomalous electrochemical corrosion of magnesium and zinc in sodium trinitride solution has been made, through predicted analogies, in the preamble. They tend to support, furthermore, the interpretation of the phenomena observed when copper is made anode in that solution. The formation of the highly explosive black compound on the anode may be explained as the result of the nitridation of the soluble cuprous trinitride to the insoluble cupric compound.

Summary.

In the reaction between hydronitric acid and cuprous oxide the acid plays the role of an oxidizing agent and is reduced to ammonia and nitrogen.

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THE ACTION OF HYDRONITRIC ACID ON CUPROUS CHLORIDE AND METALLIC COPPER.

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Cuprous Chloride.—When cuprous chloride is treated with dilute hydronitric acid it is transformed from the white, crystalline form into a bulky, yellow and flocculent condition. When the latter substance is treated with hydrochloric acid, the white crystalline condition is resumed, a fact which indicates that the reaction is reversible.

Cuprous chloride, prepared by one of the well known methods, was washed by decantation with distilled water until yellow tints began to appear. It was then treated with a 2% solution of hydronitric acid. When treated with a single portion of the acid a compound resulted which was fairly stable in the air and light, and which contained both chlorine and nitrogen. This was filtered, washed and dried without any great change in color. Portions of the dried substance dropped upon a hot plate exploded with a sharp report and a flash of green flame. When it was blown into a flame, beautiful green scintillations were produced.

A small portion of this substance was prepared for analysis in the same way as was the cuprous trinitride, as described in the foregoing paper. The results of the analyses were concordant and showed the presence in the mixture of 53.7% copper and 11.2% chlorine. As the substance must be regarded as a mixture, no importance can be attached to the analytical data.

When the cuprous chloride was treated repeatedly with fresh portions of hydronitric acid solution, a substance was formed which was quite sensitive to light and air, and resembled closely the product obtained from the interaction of cuprous oxide and hydronitric acid. A microchemical analysis of this material showed the presence of the trinitride, and the absence of the chloride ion, from which it must be concluded that the compound was the cuprous trinitride.

Small portions of the substance containing both chlorine and nitrogen, together with the solutions in which they had been formed, were left undisturbed for several weeks in test tubes closed with corks. Brilliant, black crystals, resembling jet, formed in the supernatant solution and grew radially, while the original solid slowly disappeared. The mother-liquor was green in color. Under the microscope the jet-like crystals were found to be bundles of closely packed, translucent needles, of a dark, brownish green color. A microchemical analysis showed the presence of the trinitride ion and the absence of the chloride ion—a white precipitate was produced when the vapor from the nitric acid solution of the substance came into contact with silver nitrate solution; this precipitate was soluble in nitric acid, and the addition of silver nitrate to the solution from which the vapor was evolved gave no precipitation.

Minute pieces of the needles dropped upon a hot plate exploded with a sharp snap and a flash of green flame. The compound was taken to be crystalline cupric trinitride, resulting from the gradual formation of cupric ions in the presence of the trinitride ions. Cupric trinitride has been shown to be a substance but sparingly soluble in water.[1] However, because of its explosive nature, the compound was not submitted to a quantitative analysis.

Metallic Copper.—Finely divided metallic copper was prepared from copper sulfate by precipitation with granulated zinc. On the complete

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[1] Curtius and Rissom, *J. prakt. Chem.*, **58**, 261 (1898).

precipitation of the copper, the precipitate was boiled with successive, fresh portions of dilute sulfuric acid until there was no further evolution of gas. This procedure should have insured the complete removal of all zinc.

Metallic copper, prepared as stated, was treated with a few cubic centimeters of 2% hydronitric acid. A slow evolution of gas immediately ensued. The red color of the copper gradually changed to the dark brown of the flocculent cupric trinitride. The supernatant liquid became neutral to litmus and, after about a week, deposited pale blue copper compounds, presumably basic. The addition of a drop of sodium hydroxide to the solution produced a yellow precipitate, doubtless of cuprous oxide. *Ammonia was evolved* without warming and in such amounts as to be distinctly evident to the sense of smell. Its evolution was further attested by the bluing of red litmus paper and the blackening of mercurous nitrate paper. Tests for hydrazine with Fehling's solution showed no reduction.

In order to determine the composition of the gas evolved from the action of hydronitric acid on copper, the reaction was allowed to take place in a stoppered tube and the evolved gas was conducted into a gas-holder, as described in the account of the corresponding experiment with cuprous oxide.

In twelve hours 25 cc. of gas had accumulated. This was analyzed in portions, the following values from a single analysis being typical: A sample, 17.0 cc. in volume, was added to a volume of 33.2 cc. of pure nitrogen,[1] making a total volume of 50.2 cc. Over alkaline pyrogallol there was a contraction to 49.7 cc., representing a loss in volume of 0.5 cc. Passing the gas repeatedly over palladium black, at a temperature near 100°, caused no further contraction; accordingly, it was taken to be *nitrogen.* Ammonia was found to be present in the solution resulting.

These experiments, although extremely simple, establish the fact that the reduction of hydronitric acid by metallic copper yields ammonia and nitrogen as reduction products. Copper dissolves in hydronitric acid with an effervescence of nitrogen. The ammonia resulting from the reaction neutralizes its equivalent of hydronitric acid to form ammonium trinitride. It was assumed, without analysis, that the copper became, superficially at least, the cupric trinitride.[2] The following equation is proposed to represent the reaction between copper and hydronitric acid:

$$Cu + 4HN_3 = CuN_6 + NH_4N_3 + N_2$$

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[1] From a previous analysis. The addition was merely to give a convenient volume with which to work.

[2] THIS JOURNAL, 33, 803 (1911), see p. 824.