

THE CHEMICAL NEWS.

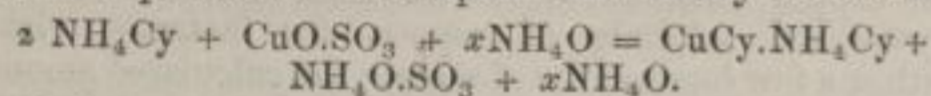
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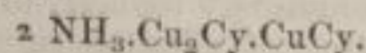
On Various Methods for the Estimation of Copper, by
FREDERICK FIELD.

[SECOND PART.]

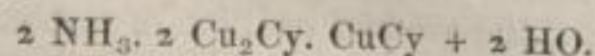
IN resuming the brief notice upon the various methods of estimating copper, it may be remarked that Dr. Mohr (*Liebig's Annalen*, May 1855, and *Chemical Gazette*, July 1855) in a paper upon the volumetric determination of hydrocyanic acid and the cyanides of the alkaline metals, recommends a solution of a copper salt added to the liquid to be tested containing excess of ammonia. The cupreous compound is added until a permanent blue colour is produced. He explains the theory as follows:



"There are, therefore," he says, "two atoms of cyanogen and one of copper in the compound. All the experiments prove the existence of the compound $\text{CuCy} + \text{NH}_4\text{Cy}$, and show that no intermediate forms are produced in the process." That Dr. Mohr is correct in asserting the existence of $\text{CuCy} + \text{NH}_4\text{Cy}$, there can be little doubt, although I believe he has not succeeded in separating it from its solution. Many experiments I made some years ago convince me that a solution of a copper salt is a very delicate test for cyanogen, and that the strength of all alkaline cyanides and solutions of hydrocyanic acid can be most readily determined, and with the greatest exactness by this means, but the concluding portion of the paragraph quoted above, in which is said, "that no intermediate forms are produced in the process," is open to discussion. When cyanide of potassium or hydrocyanic acid is added to a strong solution of an ammoniacal salt of copper, green crystals of great beauty are deposited, only soluble after some time in cold ammonia. This has often happened in an assay of rich copper ore, when the solution was not sufficiently dilute, and caused much trouble, as the crystals settle quickly and adhere slightly to the glass—this compound has been analysed by Dufau, who gives the composition



(Cyanide cuproso-cupric bi-ammoniacal), and more recently by Hilkenkamp, whose analysis leads to following formula:—



varying considerably from the results obtained by Dufau. After separating the crystals by filtration, the mother-liquid deposits brilliant violet crystalline scales of great lustre, which consist of $2 \text{NH}_3 \cdot 2 \text{Cu}_2\text{Cy} \cdot \text{CuCy}$ or the green compound minus two equivalents¹ of water (Hilkenkamp).

¹ As the separation of these two beautiful compounds is attended with some difficulty when they are both in solution in ammonia, the following

Besides these two compounds, I have met with others which I believe have not been noticed. The solution from which the green and violet crystals have separated, is of a pale blue colour, and deposits after some days hard golden coloured crystals of considerable size and beauty.

Also when hydrocyanic acid, or a soluble cyanide is added in slight excess to an ammoniacal solution of copper, so as to render it colourless, brilliant pearly crystals, some exceeding an inch in length, are deposited after the lapse of a few weeks. This compound contains much less copper than that described by Mohr. It may be further added that when cyanide of potassium is mixed in slight excess with ammoniacal copper containing a large quantity of sesquioxide of iron or other insoluble substance, in suspension, small white feathery tufts form on the surface of the precipitate, after a few hours. These crystals are very soluble in water, and bear every resemblance to cupro-cyanide of ammonium ($\text{Cu}_2\text{Cy} \cdot \text{NH}_4\text{Cy}$). All the other compounds mentioned above are perfectly insoluble in cold water; thus, even omitting the white crystalline body deposited after the solution becomes colourless, and the tufty crystals just mentioned, at least three compounds, green, violet, and yellow, are formed.

Notwithstanding this, however, it is certain that two atoms of cyanogen are necessary to decolorise one of copper in ammonia; and whatever may be the formulæ of the intermediate products, they are resolved into a compound containing two of cyanogen and one metal. Dr. Mohr mentions as a converse to the estimation of hydrocyanic acid by copper, the estimation of copper by hydrocyanic acid. That eminent chemist was probably unaware of Mr. Parkes's method published some years previously.

Appended is a table containing some results of experiments made upon pure copper, and that metal when in conjunction with some others. As this subject was treated in the last paper upon the subject, no further comment is necessary.

1000 grains of solution of cyanide of potassium exactly decolorised 10.00 copper.

				Divisions of burette in grs.
10.00	Copper		require	1000
10.00	"	+ 10 grs. of	Iron	1000
10.00	"	"	Lead	1000
10.00	"	"	Bismuth	1000
10.00	"	"	Antimony	1000
10.00	"	"	Tin	1000
10.00	"	"	Mercury	1500
10.00	"	"	Silver	1320
10.00	"	"	Zinc	1250

method employed by Mr. John Abel and myself in some researches upon the cyanides, may be adopted with advantage. On adding a solution of cyanide of potassium to a moderately strong solution of an ammoniacal salt of copper the green compound is precipitated, perfectly free from the violet. On pouring off the mother-liquid into weak hydrochloric acid di-cyanide of copper is precipitated. This substance, dissolved in weak warm ammonia, and filtered, gives the violet crystals free from the green. In attempting to obtain the former compound by gentle evaporation of the filtrate from the green crystals, a mixture of both salts nearly always occurs.—F. Field.