XIX.—*On the Action of Hydrosulphate of Ammonia upon freshly precipitated Sulphide of Copper.*

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THE circumstance that, in the ordinary course of qualitative analysis, hydrosulphate of ammonia is capable of dissolving sulphide of copper, is well known; but as I could not meet with any explanation of it, I have made some experiments which demonstrate the production of a soluble crystalline compound containing copper, sulphur, ammonia, and hydrogen, upon the formation of which the solubility of the sulphide appears to depend.

When freshly precipitated well-washed sulphide of copper (prepared from sulphate of copper and hydrosulphuric acid) was boiled for a minute or two, in a flask, with colourless freshly prepared hydrosulphate of ammonia (obtained by saturating solution of ammonia with hydrosulphuric acid, and adding an equal volume of the same ammonia), an appreciable quantity of the sulphide of copper was taken into solution.

To prove that this was not due to any sulphur accidentally mixed with the sulphide of copper, the portion left undissolved was rapidly washed, and again boiled with the colourless hydrosulphate of ammonia, when a fresh quantity was dissolved.

By boiling the sulphide of copper with hydrosulphate of am-

monia saturated with sulphur, a very large quantity could be dissolved, and the solution, when mixed with hydrochloric acid, deposited an orange coloured precipitate, very dangerously similar to that of sulphide of antimony.

When the solution of sulphide of copper in the strongly sulphuretted hydrosulphate of ammonia was allowed to stand for some hours in a well-closed bottle, it deposited very beautiful vermilion-red tufts of needles, resembling chromic acid, but of a brighter colour.

These crystals were partially decomposed by washing, the washings coming away very yellow, long after the adhering mother-liquor had been removed, and furnishing a dark green precipitate of sulphide of copper when boiled.

If the partially washed crystals were rapidly dried over oil of vitriol, they assumed a fine copper-red colour, and suffered very little decomposition; but, in the moist state, they decomposed rapidly, evolving an ammoniacal odour, and becoming black. They suffered the same change in the water-oven.

On heating the crystals (dried over oil of vitriol) in a tube, they evolved a trace of moisture, and abundance of hydrosulphate of ammonia (judging by the smell), leaving a black residue, which evolved much sulphur when further heated.

Gently heated with water, the bulk of the crystals dissolved, leaving a black residue. The yellow solution became dark green and turbid on standing, and gave a black precipitate with hydrochloric acid.

Hydrochloric acid did not act upon the crystals in the cold, but, when heated, much hydrosulphuric acid was evolved, and a black residue left. No separation of sulphur was perceptible.

Nitric acid was also without action upon the crystals until heat was applied, when violent oxidation took place, and much sulphur was separated.

The analysis of the compound was effected by boiling with nitric acid until the sulphur had separated in pure yellow globules, which were collected and weighed.

The filtrate and washings from the sulphur were precipitated by chloride of barium, and the dissolved sulphur calculated from the weight of the sulphate of baryta. The filtrate from this last was precipitated by sulphuric acid, and after removing the sulphate of baryta, the copper was precipitated by boiling with potash.

The ammonia was determined in a separate portion by boiling

with hydrochloric acid till the compound was completely decomposed, removing the small quantity of dissolved copper from the solution by hydrosulphuric acid, and evaporating the filtered liquid, the residue of hydrochlorate of ammonia being carefully dried and weighed.

From the evolution of hydrosulphuric acid under the action of hydrochloric acid, it was inferred that the ammonia was associated with an equivalent of hydrogen, and it was therefore calculated as NH_4 .

One of the specimens analysed had been rapidly dried over oil of vitriol, and the other by repeated pressure between folds of blotting-paper.

The results of the analysis were :—

		Calculated ($\text{Cu}_2\text{NH}_4\text{S}_7$ *)	
Cu....	32·65	32·11	32·81
S....	58·07	59·07	57·88
NH_4	9·07	8·82†	9·31
	<hr/> 99·79	<hr/> 100·00	<hr/> 100·00

The formula which most nearly corresponds with these numbers, with a divergence which is scarcely to be avoided in dealing with a compound of this nature, would be $\text{Cu}_2\text{NH}_4\text{S}_7$.

Speculating upon the constitution of the compound, the two simplest rational formulæ which present themselves are $2\text{CuS}_3 \cdot \text{NH}_4\text{S}$ and $2\text{CuS} \cdot \text{NH}_4\text{S}_5$.

The mode of producing the compound would, of course, favour the latter formula, but I am inclined to prefer the former, because (1) there is no sign of the separation of sulphur on treating with hydrochloric acid; (2) of the absence of action on the part of cold nitric acid (conc.); and (3) of the action of heat upon the crystals.

In works upon qualitative analysis, it is often recommended that sulphide of potassium be substituted for hydrosulphate of ammonia as a solvent for the sulphur-acids existing in the hydrosulphuric acid precipitate, when copper is at all likely to be present; but I have often found that copper which might have been overlooked in the analysis of a large mass of the remaining basic sulphides (*e.g.*, of bismuth and lead) has been easily detected, in consequence of its having passed out in the

* $\text{Cu} = 31\cdot7$ $\text{NH}_4 = 18$ $\text{S} = 16$.

† By difference.

hydrosulphate of ammonia solution, where it does not interfere with the investigation for arsenic, antimony, and tin.