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AMMONIUM SELENIDE.

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BY bringing ammonia and hydrogen selenide together Bineau[1] claims to have prepared ammonium selenide. His product was a white, crystalline solid, which was readily decomposed by water in the presence of air. No mention occurs anywhere that this compound was ever obtained by crystallization from solution, hence it may be of interest to note that when prepared by the latter method it crystallizes in black, anhydrous, orthorhombic prisms. Peculiar conditions, however, seem necessary for its formation. Thus, in attempting to make ammonium selenomolybdate it was observed that when an ammoniacal solution of ammonium molybdate was saturated with hydrogen selenide gas a dark-red colored solution resulted, which yielded the black crystals of ammonium selenide upon careful evaporation. The solution contained five grams of ammonium molybdate in fifty cc. of water, to which twenty cc. of the strongest ammonia water had been added. The solution was saturated with hydrogen selenide gas. The resulting liquid, deep red in color, was concentrated in a vacuum over sulphuric acid. The final residue consisted of ammonium molybdate, metallic selenium, and well-defined, black, orthorhombic crystals. The latter were separated as completely as possible from the selenium, and extracted for several days with pure carbon disulphide. The crystalline mass, purified as far as possible in this manner, proved to be stable in the air, and dissolved readily in water to a dark-red colored solution. The latter, when freshly made, precipitated selenides from neutral or alkaline solutions of metallic salts. On exposure to the air, however, the solution of the salt suffered decomposition with the separation of black selenium. An excess of ammonia seems not to prevent the change.

The analysis gave as follows :

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[1] *Ann. chim. phys.*, [2], 67, 227.

I. 0.3051 gram of substance gave 0.2137 gram selenium = 70.04 per cent. selenium.

II. 0.2031 gram of substance gave 0.1418 gram of selenium = 69.81 per cent. selenium.

Ammonium.

III. 0.2012 gram of substance gave 0.0603 gram of ammonium = 29.97 per cent. ammonium.

IV. 0.3036 gram of substance gave 0.0918 gram of ammonium = 30.24 per cent. ammonium.

The discrepancy between the found and calculated percentages is due to metallic selenium, which adhered to the ammonium selenide crystals. The salt was distilled with sodium hydroxide in determining the ammonium content. The liberated ammonia was absorbed by standard hydrochloric acid, the excess of the latter being titrated with standardized alkali.

In estimating the selenium a weighed quantity of the salt was dissolved in water containing a little sodium hydroxide. An excess of hydroxylamine[1] hydrochloride was added to this solution, from which the selenium separated completely after boiling several minutes. It was then transferred to a weighed Gooch filter, washed with water and dried at 105° for one hour. This method is far superior to the usual course of precipitating selenium by means of sulphurous acid.

The ammoniacal molybdate solution of the strength given in the preceding lines is the only solution from which the black crystals were obtained. Under these conditions the salt was always found, but with molybdate solutions of greater dilution or with such as contained arsenic acid or tungstic acid, evaporation showed nothing but metallic selenium.

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[1] Privately communicated by Dr. H. F. Keller.