After all, though, if work of this type has any value it is not so likely to lie in the actual results obtained by the first attempt as in the general suggestion it offers for such studies of the more important analytical reactions. It is at any rate the intention in this laboratory to carry out other investigations of a similar kind.

Summary.

In this article there has been described:

1. The preparation of pure magnesium salt for use as a standard in analytical work.

2. An easily constructed piece of apparatus by which material can be heated in a combustion tube and transferred to a weighing bottle without exposure to the air.

3. A set of experiments in which anhydrous magnesium chloride was transformed into magnesium sulfate.

Columbus, O.

BEHAVIOR OF AMMONIUM PHOSPHOMOLYBDATE WITH AMMONIUM HYDROXIDE.

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In the Woy[1] method of estimation of phosphates, the phosphoric acid is first precipitated as ammonium phosphomolybdate, which is then dissolved in ammonia and reprecipitated by magnesia mixture. Evidently, in solution, free phosphate ions exist.

Gibbs[2] has made a thorough investigation of these reactions and he has shown that the ammonium phosphomolybdate dissolves in ammonia and on allowing the ammoniacal solution to stand, glistening needles or prisms, having the composition $2(NH_4)_3PO_4.5MoO_3.7H_2O$ separate out. The present investigation was undertaken for a fuller study of the solubility of ammonium phosphomolybdate in ammonium hydroxide. A pure sample of ammonium phosphomolybdate was prepared by precipitating a solution of sodium-hydrogen phosphate with ammonium molybdate. The precipitate was then washed free from mother liquor and dried. The dry yellow powder was placed in a beaker and an excess of strong solution of ammonia was added to it and stirred; a white crystalline salt was at once thrown down with evolution of heat.

This white substance was immediately dried by pressing between the folds of bibulous drying paper and analyzed. The substance was not put in a desiccator but dried in air.

Calc. for $(NH_4)_2Mo_2O_7.3NH_3$: Mo = 49.11; N = 17.88; H = 4.42; found: Mo = 49.8; N (by Kjeldahl) = 17.25; H (by combustion) = 4.15.

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[1] *Chem. Ztg.*, **21**, 442.

[2] *Am. Chem. J.*, **5**, 361, 391, etc.

A dozen preparations were undertaken in which the strength of ammonia was varied, but invariably the same crystalline substance was obtained, as was determined by quantitative analysis.

That it was not a mixture of two or more substances was proved in the following way: A sample, freshly prepared, was taken at random, carefully washed with distilled water, dried and analyzed.

Found for washed portion: Mo = 49.22; NH_3 (by Kjeldahl) = 20.6; found for unwashed portion: Mo = 49.35; NH_3 (by Kjeldahl) = 20.7.

Thus we see that a definite compound, having the composition

$$(NH_4)_2Mo_2O_7.3NH_3,$$

is obtained as precipitate by adding strong solution of ammonia to ammonium phosphomolybdate. It has been found, however, that the substance gradually loses ammonia and if we put the salt in a weighing tube it very gradually loses weight and the smell of ammonia is given off. At the same time the crystals crumble to a white powder. Moreover, that the ammonia in the compound is loosely combined is shown by its peculiar behavior in the determination of nitrogen. On heating the substance during analysis about three-fifths of the total nitrogen is immediately given off and the remaining two-fifths is collected after a long time on prolonged heating. That the salt of the composition $(NH_4)_2Mo_2O_7.3NH_3$ gradually loses ammonia was shown by the following comparative tests:

0.1870 g. of the salt gave, by the Kjeldahl method, 0.0383 g. of ammonia, or 20.5%.

On the very next day 0.5249 g. of the same sample gave 0.1029 g. of NH_3, or 19.6% ammonia.

The final and stable product of decomposition was then carefully analyzed:

Calc. for $(NH_4)_2Mo_2O_7$: Mo = 56.48; N = 8.23; H = 2.48; found: Mo = 56.35; N (Dumas method), 7.8; H (by combustion), 2.81.

Hence the substance $(NH_4)_2Mo_2O_7.3NH_3$ obtained as precipitate decomposes into the dimolybdate $(NH_4)_2Mo_2O_7$. But sometimes a little phosphoric acid, varying from 0.1 to 0.2%, has been found, which is probably adsorbed with the crystals.

If the ammonia used is very dilute we do not get an immediate precipitation on its addition to ammonium phosphomolybdate, but if the solution is allowed to evaporate, generally at first crystals of ammonium molybdate, having the composition $(NH_4)_2Mo_2O_7.3NH_3$, separate out. Very seldom we get the salt described by Gibbs.

But if we add a large excess of strongest solution of ammonia available, at first the same crystalline substance is obtained, which on further addition of ammonia dissolves, and after a short time a gelatinous, flocculent precipitate appears. After vigorously stirring and allowing to settle, a precipitate thus obtained was then drained from the mother liquor by strong suction and dried by means of blotting paper. It was extremely hygroscopic. The precipitate was found to be absolutely free from molybdate. On analysis it gave the following results:

Calc. for $(NH_4)_2HPO_4$: PO_4 = 71.99; N = 21.3; H = 6.8; found: PO_4 = 71.86: N (Dumas) = 21.9; H = 6.5%.

Evidently on adding a large excess of strong solution of ammonia the salt of the composition $(NH_4)_2HPO_4$ is obtained. Now the dimolybdate $(NH_4)_2Mo_2O_7$ is rather sparingly soluble and the substance $(NH_4)_2Mo_2O_7.3NH_3$ is much more soluble, but on adding excess of ammonia, evidently a compound containing ammonia much in excess to the compound described above is formed which is very easily soluble and hence remains in solution and only ammonium hydrogen phosphate is precipitated. These relations will be clear from Table I.

TABLE I.

Specific gravity of ammonia used.	Weight of ammonium phosphomolybdate taken. Grams.	Volume of the solution of ammonia used. Cc.	Observation.
0.90	9.5	40	Extremely hygroscopic crystals of $(NH_4)_2HPO_4$ were obtained as precipitate.
0.91	9.45	25	Prismatic crystals of $(NH_4)_2Mo_2O_7.3NH_3$ were obtained as precipitate.
0.92	9.5	14	No precipitate: but on allowing the ammoniacal solution to evaporate, first, all the molybdenum appears as $(NH_4)_2Mo_2O_7.3NH_3$ and then phosphoric acid as $(NH_4)_2HPO_4$.

Incidentally, crystals of ordinary ammonium molybdate were analyzed and it was found to correspond to the formula $(NH_4)_6Mo_7O_{24}.4H_2O$.

Calc. for $(NH_4)_6Mo_7O_{24}.4H_2O$: Mo = 54.37; N = 6.8; found: Mo = 54.37; N = 7.38.

Summary.

The addition of ammonium hydroxide of medium strength to ammonium phosphomolybdate usually produces a crystalline deposit having the composition $(NH_4)_2Mo_2O_7.3NH_3$, on the addition of strongest ammonium hydroxide available, hygroscopic crystals of the composition $(NH_4)_2HPO_4$ are obtained.

In conclusion, I offer my best thanks to Professors Ray and Bhaduri.

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