

NEW METHODS FOR THE PREPARATION OF SALTS OF SELENIC ACID.

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The purpose of this paper is to describe the preparation of metallic selenates from ammonium selenate. Ammonium selenate is the best starting material on account of the very satisfactory method¹ by which it may be prepared. An outline of the method for preparing ammonium selenate is as follows: Selenic acid was first prepared by oxidizing a solution of selenium in nitric acid with potassium permanganate. This solution after the removal of the manganese dioxide precipitate by filtration was precipitated with lead nitrate. The lead selenate thus formed was washed thoroughly until free from soluble salts. The treatment of this solid lead selenate with an excess of a strong solution of ammonium carbonate produced lead carbonate and ammonium selenate in solution. Pure ammonium selenate crystallized from the filtrate upon evaporation while the excess of ammonium carbonate was volatilized.

There are three methods by which this ammonium selenate may be changed into metallic selenates. They are as follows:

1. The crystallization of a solution of ammonium selenate with a metallic nitrate will give crystals of the most insoluble salt which can be formed by any combination of the four ions in solution. The most soluble combination of the ions will remain in the mother liquor. The solubility of the possible combinations of the four ions is in this order beginning with the most soluble, ammonium nitrate, metallic nitrate, ammonium selenate, and ammonium metallic selenate or metallic selenate. Whether the metallic selenate or the double ammonium salt is formed depends upon their relative solubility except that by increasing the amount of ammonium selenate the double salt may be produced in cases where the metallic salt is ordinarily formed. For example, equivalent amounts of ammonium selenate and copper nitrate give copper selenate while two equivalents of the ammonium selenate to one of copper nitrate gives the ammonium copper selenate.

¹ Mathers and Bonsib, *Jour. Amer. Chem. Soc.*, 33,703 (1911); *Indiana University Studies*, 841 (1910).

The following table shows the quantities of materials used, the salts formed and the yields :

Weight of ammonium selenate used.	Formula of nitrate and grams used.	Molecules of ammonium selenate to one of the nitrate.	Formula of Salt formed.	Grams of salt formed.	Theoretical yield.
30.....	Cu (NO ₃) ₂ ·3H ₂ O.58	1 : 1	Cu SeO ₄ ·5H ₂ O.....	49.6	50.
40.....	NiONO ₃ ·6H ₂ O.32.	2 : 1	NH ₄ ·Ni (SeO ₄) ₂ ·6H ₂ O.....	48.5	54.
40.....	Co(NO ₃) ₂ ·6H ₂ O.32.	2 : 1	NH ₄ ·Co (SeO ₄) ₂ ·6H ₂ O.....	52.1	54.
40.....	Mn(NO ₃) ₂ ·6H ₂ O.32.	2 : 1	NH ₄ ·Mn (SeO ₄) ₂ ·6H ₂ O.....	52.1	54.
20.....	Zn(NO ₃) ₂ ·6H ₂ O.33.	1 : 1	NH ₄ ·Zn (SeO ₄) ₂ ·6H ₂ O.....	27.1	27.6
20.....	Al(NO ₃) ₃ ·9H ₂ O.42	2 : 1	NH ₄ Al (SeO ₄) ₂ ·12H ₂ O.....	115.	122.

The following table shows the volume of the solution used in the preparation of each selenate, the amount of selenate present, and the amount which crystallized upon standing over night. This table gives an idea of the relative solubility of these selenates and shows the volumes of solution to use in preparing them:

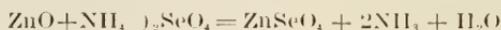
TABLE IV.

Formula of salt crystallized.	Weight of Salt Present.	Volume of solution.	Weight of Salt Crystallized.
CuSeO ₄ ·5H ₂ O.....	49.63 grams.....	150 C.C.....	18 grams.
Ni·NH ₄ ·(SeO ₄) ₂ ·6H ₂ O.....	48.52 grams.....	225 C.C.....	4.93 grams.
Co·NH ₄ ·(SeO ₄) ₂ ·6H ₂ O.....	52.60 grams.....	98 C.C.....	4.42 grams.
Mn·NH ₄ ·(SeO ₄) ₂ ·6H ₂ O.....	52.12 grams.....	65 C.C.....	9.80 grams.
Zn·HN ₄ ·(SeO ₄) ₂ ·6H ₂ O.....	27.10 grams.....	110 C.C.....	8.13 grams.
Al·NH ₄ ·(SeO ₄) ₂ ·12H ₂ O.....	115.00 grams.....	150 C.C.....	13.52 grams.

The following table gives the results of analyses which were made to determine the formulas of the salts:

Formula.	Per cent Found		Per cent. From Theory.	
	NH ₃	Metal.	NH ₄	Metal.
CuSeO ₄ ·5H ₂ O.....		21.5		21.4
NH ₄ ·Ni (SeO ₄) ₂ ·6H ₂ O.....	6.7	11.9	6.9	12.
NH ₄ ·Co (SeO ₄) ₂ ·6H ₂ O.....	6.8	12.3	6.7	12.
NH ₄ ·Mn (SeO ₄) ₂ ·6H ₂ O.....	6.9	11.3	7.0	11.3
NH ₄ ·Zn (SeO ₄) ₂ ·6H ₂ O.....	6.6	13.2	7.1	13.6
NH ₄ Al (SeO ₄) ₂ ·12H ₂ O.....	3.1	4.9	3.1	4.9

2. Ammonium selenate can be decomposed by basic metallic oxides with the formation of the metallic selenate and volatilization of the free ammonia. For example:



Zinc oxide was selected because of its pronounced basic properties. Ammonium selenate, dissolved in water, was treated with an excess of zinc oxide. The evolution of ammonia was slow at room temperature but was more rapid at the boiling point. Zinc selenate and not the double salt was obtained by crystallization of the solution. The yield was only about 25 per cent. of the theory. Analysis of the $\text{ZnSeO}_4 \cdot 7\text{H}_2\text{O}$ showed 18.8 per cent. zinc while the theory is 19.4.

3. This method makes use of copper selenate prepared as described above. Any metal more electropositive than copper will precipitate copper from a copper selenate solution and form a selenate of the metal that was used. This is the best method of making the metallic selenates since a pure solution of the metallic selenate can be obtained. The previous preparation of the copper selenate from the ammonium selenate is exceptionally easy. Selenates of cadmium and zinc were prepared by treating solutions of 15 grams copper selenate dissolved in 50 cc. of water with an excess of metallic cadmium and metallic zinc respectively. The yield of cadmium selenate was 14.1 grams and of zinc selenate 16.7 grams while the theory was 14.7 and 16.3 respectively.

SUMMARY.

Ammonium selenate, on account of the very satisfactory method for its preparation, is the most suitable starting material for the making of metallic selenates. The three methods that were tried for preparing metallic selenates from ammonium selenate are:

1. Crystallization of a solution containing ammonium selenate and a metallic nitrate will produce crystals of the double ammonium selenate (or the metallic selenate in some cases) since this salt is the most insoluble which can be produced by any possible combination of the four ions. The yields are good.

2. Ammonium selenate can be decomposed by basic metallic oxides with the formation of the metallic selenate and of free ammonia. This is not a satisfactory method and the yields are low.

3. The treatment of copper selenate solution with any metal which is more electropositive than copper will precipitate metallic copper and form the corresponding metallic selenate. This is a very satisfactory method and the yields are practically quantitative.

