Summary.

1. A reliable method has been devised for the preparation of pure lead hydrogen arsenate.

2. All attempts to prepare pure lead orthoarsenate have been unsuccessful.

3. Lead pyroarsenate has been prepared.

4. A new basic lead arsenate of apparently constant composition has been obtained.

5. The specific gravity of lead hydrogen arsenate and basic lead arsenate have been determined.

6. The difficulties attending the accurate determination of the solubility of the compounds prepared have been pointed out. The tests made, however, show these substances to be relatively insoluble.

7. A quantitative method has been devised for the estimation of lead hydrogen arsenate in mixtures of this substance with the basic arsenate.

8. The results show that the precipitates obtained from the reactions of lead acetate and lead nitrate with di-sodium hydrogen arsenate under certain conditions are mixtures of lead hydrogen arsenate and the basic lead arsenate.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

THORIUM AMMONIUM OXALATE.

BY C. JAMES, C. F. WHITTEMORE AND H. C. HOLDEN.

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Bahr[1] found that thorium oxalate dissolved in a warm solution of ammonium oxalate, and Bunsen[2] showed that this reaction might be employed for separating thorium from the rare earths.

Brauner[3] investigated the subject more thoroughly and showed that, when thorium oxalate was dissolved by ammonium oxalate, a definite ammonium thoroxalate was formed, to which he ascribed the formula $Th(C_2O_4.NH_4)_4.7H_2O$. This hydrate was said to separate from a supersaturated solution, while a lower hydrate possessing four molecules of water was obtained by spontaneous evaporation. When the ammonium thoroxalate was treated with water, it was hydrolyzed. The resulting product was very colloidal and passed through filter paper. It required two months time in order to settle. Later, however, a precipitate was obtained that became crystalline. These crystals possessed the formula $2Th(C_2O_4)_2.(NH_4)_2C_2O_4.7H_2O$.

The writers decided that a study of the solubility curves of thorium

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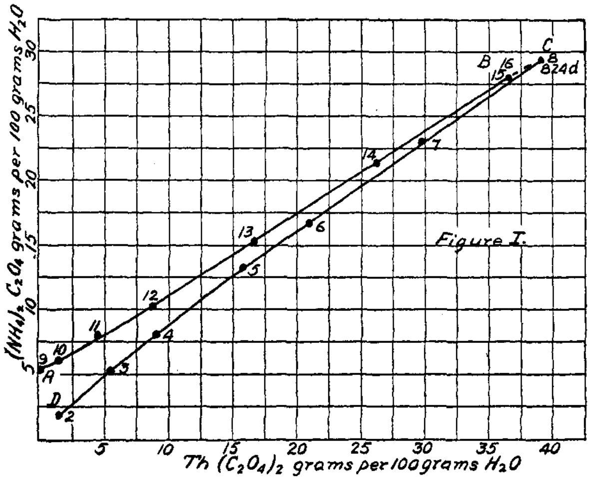
[1] *Ann.*, **132**, 231.

[2] *Ann. Phys. Chem.*, **155**, 375.

[3] *J. Chem. Soc.*, **73**, 951.

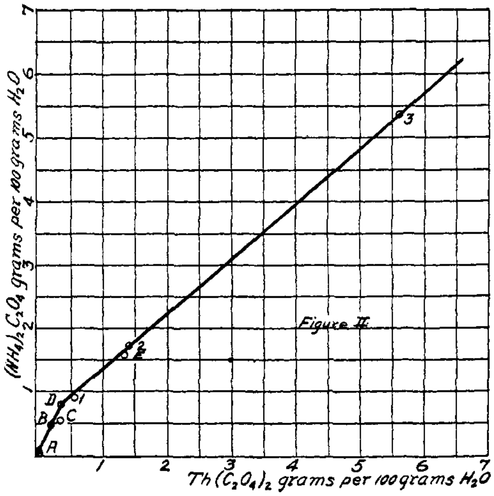
oxalate and ammonium oxalate, in the presence of each other in water, would show clearly and distinctly the number and kinds of compounds existing. This work was commenced in 1912, and it appears O. Hauser started work along similar lines at a similar date.[1]

In order to determine the various solubilities, several bottles were prepared and placed in a thermostat at 25°. They contained varying amounts of thorium oxalate and ammonium oxalate with sufficient water to make 50 cc. After rotating for many weeks, the bottles were allowed to stand at the same temperature until the supernatant liquid became clear, when portions were withdrawn for analysis. In each of the samples, thorium oxide and C_2O_3 were determined. The thorium content was obtained by evaporating a weighed portion of the solution in a tared platinum dish, and igniting the residue to oxide. The C_2O_3 was found by titrating with a standard potassium permanganate solution.



The results are given in Table I, and plotted in Fig. 1.

The data when plotted are not quite sufficient to complete the curve. No points were obtained between *B* and *C*, which are evidently transition points. Later, it was found that the solid phase, in the bottles from 2 to 8 along that portion of the curve *CD*, consisted of a definite compound. It, therefore, became necessary to follow the curve more completely between the points *B* and *C* and from bottle 2 to the zero point. More bottles were, therefore, pre-



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[1] R. J. Meyer und O. Hauser, "Analyse der seltenen Erden und Erdsäuren," p. 167.

pared and rotated for several months in a thermostat at 25°. It was necessary to rotate for a considerable length of time; otherwise, results of a metastable condition would be obtained. The data are given in Table II and plotted in Fig. 2.

TABLE I.

Bottle No.	$(NH_4)_2C_2O_4$. Per cent.	$Th(C_2O_4)_2$. Per cent.	G. $(NH_4)_2C_2O_4$ per 100 g. H_2O.	G. $Th(C_2O_4)_2$ per 100 g. H_2O.
1	0.89	0.57	0.90	0.58
2	1.65	1.38	1.70	1.42
3	4.83	5.06	5.36	5.63
4	6.93	7.79	8.13	9.13
5	10.27	12.35	13.27	15.96
6	12.20	15.35	16.84	21.18
7	15.07	19.54	23.04	29.87
8	17.49	23.19	29.47	39.10
9	4.98	...	5.25	...
10	5.62	1.43	6.04	1.54
11	6.93	4.07	7.78	4.51
12	8.70	7.40	10.37	8.82
13(*a*)	11.68	12.76	15.46	16.89
13(*b*)	11.68	12.77	...	...
14	14.52	17.84	21.47	26.37
15	17.11	22.18	28.18	36.54
16	17.13	22.16	28.21	36.51
8(*z*)	17.49	23.19	...	...
4(*d*)	Results of analysis identical with those of 8(*z*)			

TABLE II.

Bottle No.	$(NH_4)_2C_2O_4$. Per cent.	$Th(C_2O_4)_2$. Per cent.	G. $(NH_4)_2C_2O_4$ per 100 g. H_2O.	G. $Th(C_2O_4)_2$ per 100 g. H_2O.
A	0.03	0.03	0.03	0.03
B	0.48	0.20	0.48	0.20
C	0.52	0.36	0.52	0.36
D	0.79	0.35	0.80	0.35
E	1.50	1.31	1.54	1.35

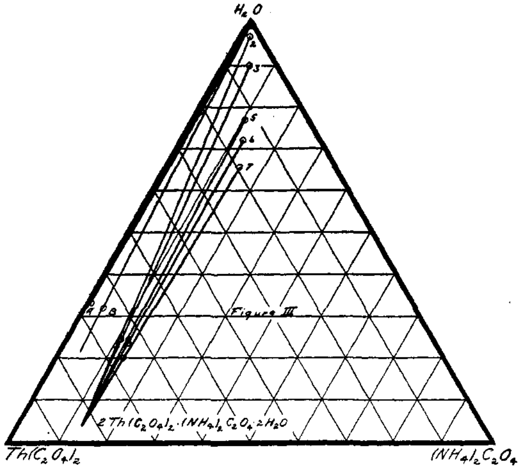
Points 1, 2 and 3 are taken from Table I, and are the same as in Fig. 1.

TABLE III.

Solid Phase.

Bottle No.	$(NH_4)_2C_2O_4$. Per cent.	$Th(C_2O_4)_2$. Per cent.
2	10.51	66.39
3	10.84	64.77
5	12.78	63.98
6	12.65	63.87
7	13.40	66.42
A	0.00	66.89
B	3.17	64.85

Unfortunately, no new points came between *B* and *C*. Samples of the solid phase, along that part of the curve from *C* in Fig. 1 to *A* in Fig. 2, were withdrawn by means of a platinum spoon, and freed as much as pos-



sible from the mother liquor by pressing between filter papers in a screw press. The pressed sample was quickly transferred to a weighing bottle and thoroughly mixed.

The thorium oxide and C_2O_3 contents were then determined.

The data are given in Table III and plotted in Fig. 3.

It will be seen that lines joining the points of the corresponding liquid and solid phases meet at a common point, expressed by the formula $2Th(C_2O_4)_2.(NH_4)_2C_2O_4.2H_2O$. This does not entirely agree with the results obtained by O. Hauser, since he finds three molecules of water present. However, the authors give the formula as obtained by the triangular diagram, and not from the analysis of the pure compound.

That portion of the curve in Fig. 1 represented by the line *AB* shows the solubility of thorium oxalate in ammonium oxalate. *B* and *C* are evidently transition points and the solid phase occurring in any bottles coming between these points should consist of the normal compound, $2Th(C_2O_4)_2.(NH_4)_2C_2O_4.7H_2O$, as described by Brauner. From point *C* in Fig. 1 to point *D* in Fig. 2, there exists, as the solid phase, the compound shown in the triangular diagram. From *D* to *A* in Fig. 2, the solid phase consists of thorium oxalate. Lines joining the corresponding points, representing the liquid and solid phases, do not meet.

This work indicates that at 25° there are only two ammonium thoroxalates.

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THERMOELEMENT INSTALLATIONS, ESPECIALLY FOR CALORIMETRY.

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For maximum precision in calorimetry, electrical thermometers are essential, and they are often considered to be also the most convenient. Among them the least exacting, the most accurate for small intervals, and the freest from sources of error is the multiple thermoelement when used with a small temperature difference between its two ends. With it the relative precision required in the electrical measurement is ordinarily