ores. E. Knecht[1] fuses 0.5–1.0 g. of the mineral (*e. g.*, rutile) for 10 minutes with 10 parts by weight of potassium hydroxide, after which he washes the mass into a beaker containing a large excess of hydrochloric acid.

A method far better suited to our purpose was suggested to us by Professor W. A. Noyes.[2] According to this, the finely powdered ore is mixed with 1 part, by weight, of potassium fluoride and 5 or 6 parts of potassium pyrosulfate and fused in a platinum crucible for 15–20 minutes, until effervescence ceases. The cooled mass is then readily dissolved by hydrochloric acid to a clear solution which is ready for reduction.

With solutions prepared in this way, the ferric chloride volumetric method gave the following independent values: 34.63, 34.47, 34.44, and 34.42% of TiO_2 (mean value = 34.49%). The reduction in this case also requires not more than two hours.[3]

The ferric chloride method is thus seen to compare very favorably with the tedious gravimetric method of Gooch, and it is incomparably shorter. Such metals as tin, chromium, vanadium, tungsten, and molybdenum must, however, be absent when the solution is reduced with zinc.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OREGON AGRICULTURAL EXPERIMENT STATION.]

THE ARSENATES OF LEAD.[4]

BY HERMAN V. TARTAR AND R. H. ROBINSON.

Received June 17, 1914.

Introduction.

Some of the arsenates of lead are widely used at present as stomachic insecticides. The general properties of these compounds seem to specially adapt them for this purpose and for this reason they have been used more extensively in recent years than any other arsenical. In response to the demand for these materials, their commercial manufacture has now reached large proportions and a number of manufacturing chemists in the United States are making them in considerable quantity. This extended use of certain of the arsenates of lead for insecticidal purposes

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[1] *Z. angew. Chem.*, 26, 734–5 (1913). Knecht dilutes the HCl solution to 250 cc. and reduces a 25 cc. portion of it with granulated zinc and hydrochloric acid for 10–20 minutes, until the zinc is completely dissolved. He then suspends a zinc rod in the hot solution by means of a platinum wire which is passed through the Bunsen valve, and allows the solution to cool; finally he passes in carbon dioxide and titrates with ferric alum.

[2] *J. Anal. Appl. Chem.*, 5, 39 (1891).

[3] Since in all cases good results were obtained after 2 hours' reduction, that time is to be considered sufficient. While in some cases less time might suffice, it is safer always to allow at least 2 hours for the reduction.

[4] Presented at the Cincinnati meeting of the American Chemical Society, April, 1914.

makes a thorough knowledge of their constitution and properties, as well as analytical methods necessary to the valuation of the same, of considerable practical importance.

In connection with some other investigations on insecticides, a study of the preparation and properties of the different arsenates of lead was begun in this laboratory early in 1913. This study has been continued, as opportunity permitted, up to the present time. We have now sufficient data from which to draw certain conclusions, which are presented herewith.

Historical.

But little attention was given to the arsenates of lead previous to their use as insecticides. Lead orthoarsenate, $Pb_3(AsO_4)_2$, is reported to have been prepared by Mitscherlich[1] by the use of the reaction of di-sodium hydrogen arsenate, Na_2HAsO_4, with basic lead acetate, or with neutral lead salts. It is also stated that this substance was prepared by Berzelius[2] by the action of ammonia on lead pyroarsenate, $Pb_2As_2O_7$. The substance obtained was a white amorphous powder.

According to Mitscherlich and Berzelius,[3] lead pyroarsenate is precipitated when lead chloride or lead nitrate react in aqueous solution with arsenic acid; also as a precipitate resulting from the reaction of di-ammonium hydrogen arsenate, di-potassium hydrogen arsenate, or di-sodium hydrogen arsenate with lead nitrate in excess. It is also stated by the authority cited that Salkowski prepared this substance by the use of the reaction of neutral lead acetate and di-sodium hydrogen arsenate and that it is a white, easily melted, amorphous powder. On the whole, the work of these early investigators is very imperfect and in some instances contradictory.

Moulton,[4] chemist of the Massachusetts Gypsy Moth Commission, was the first to prepare lead arsenate for use as an insecticide. For this purpose he used lead acetate and di-sodium arsenate.

The work of Moulton was continued by Smith,[5] who studied the reactions involved and other matters pertaining to manufacture. "He stated that the ordinary spray material was not a single salt, but a mixture of neutral, $Pb_3(AsO_4)_2$, and acid, $PbHAsO_4$, arsenates, and believed that the relative amount of each depended principally upon the source of the soluble lead salt, although temperature and concentration at the moment of precipitation affected the results; in other words, the acetate

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[1] Dammer: "Handbuch der Anorganischen Chemie," Vol. 2, Pt. 2, p. 565.

[2] *Ibid.*

[3] *Ibid.*, p. 566.

[4] *Mass. Board Agr. Report*, 41, 282 (1894).

[5] *Ibid.*, 45, 357 (1898).

of lead has a tendency, other factors being equal, to yield the neutral salt and the nitrate the acid salt."[1]

Smith also states that the specific gravity of arsenate of lead is 1.00668 (salt not specified).

Haywood[2] claims that the reaction between lead acetate and di-sodium arsenate takes place as represented by the following equation:

$$3Pb(C_2H_3O_2)_2 + 2Na_2HAsO_4 \longrightarrow Pb_3(AsO_4)_2 + 4NaC_2H_3O_2 + 2CH_3COOH$$

He also found that the reaction between lead nitrate and di-sodium arsenate takes place in the main as follows:

$$Pb(NO_3)_2 + Na_2HAsO_4 \longrightarrow PbHAsO_4 + 2NaNO_3$$

The slight variation in the resulting compound from the theoretical composition of lead hydrogen arsenate caused Haywood to suggest that some unknown secondary reaction took place to small extent.

Haywood and McDonnell[3] state that, when pure lead nitrate and di-sodium arsenate are used, the reaction represented by the second equation given in the preceding paragraph proceeds almost according to theory, though a small amount of lead orthoarsenate is usually formed. They also hold that when lead acetate is used a product is obtained at times which is principally lead hydrogen arsenate. They corroborate Smith's[4] statement that the reaction is affected by various conditions, such as concentration, temperature, etc.

Volck[5] devised a quanitative method for the detection of lead hydrogen arsenate in the presence of the lead orthoarsenate. He also proposed the preparation of the orthoarsenate by the use of the reaction of lead hydrogen arsenate with ammonium hydroxide, although he admitted that the samples prepared in this manner contained somewhat less than the theoretical percentage of arsenic oxide. From his experiments, Volck further concluded that the lead hydrogen arsenate hydrolyzes easily to form the orthoarsenate, and that commercial lead arsenate might contain pyroarsenate as a component.

Holland and Reed[6] state that they prepared the orthoarsenate by precipitation, under certain conditions, from dilute solutions of lead acetate and di-sodium arsenate. In proof of this they showed that the amounts of lead and arsenic found in the precipitates corresponded closely to the theoretical composition of the lead salt. These investigators also state that lead hydrogen arsenate "is readily prepared from nitrate of lead and di-sodium hydrogen arsenate, provided dilute solutions are employed

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[1] Holland and Reed, Twenty-fourth Ann. Report Mass. Agr. Exp. Sta.

[2] *Bull.* **105**, Bur. of Chem., U. S. Dept. Agr.

[3] *Ibid., Bull.* **131**.

[4] *Loc. cit.*

[5] *Science,* **33**, 868 (1911).

[6] *Loc. cit.*

and the sodium salt is added carefully in excess (10%). By this method of procedure no difficulty was experienced in producing salts of theoretical composition."

Space will not be taken at this time to go into any extensive criticism of the work that has been done; this will be brought in the discussion of the results presented below. Taken as a whole, the literature indicates that there are at least two common lead arsenates, lead hydrogen arsenate and lead orthoarsenate; that these two compounds are the main components present in ordinary commercial lead arsenate; that lead pyroarsenate may possibly be present in the commercial salts; and that there is very little accurate knowledge of the preparation and the chemical and physical properties of the pure compounds.

Experimental.

The work completed in this laboratory has been done along special lines which a study of the literature and a consideration of the agricultural use of commercial arsenate of lead indicated to be of most immediate value. The specific points studied naturally fall under five different heads: (1) the preparation of lead hydrogen arsenate, (2) the results of attempts to prepare lead orthoarsenate, (3) the preparation of lead pyroarsenate, (4) the specific gravity and solubility of lead hydrogen arsenate and basic lead arsenate, and (5) the quantitative estimation of lead hydrogen arsenate in the presence of the basic arsenate.

(1) Preparation of Lead Hydrogen Arsenate.

The preparation of this substance was first tried by using the reaction between lead nitrate and di-sodium hydrogen arsenate. Both concentrated and dilute solutions were employed, using the reacting equivalents of the different substances and also one or the other in excess. Many attempts were made and, in some instances, the salts obtained approximated the theoretical composition very closely but not within the experimental error of analysis. Our experiments showed that very slight changes of condition affect the nature of the reaction. After much work had been done it was decided that this method could not be used safely to prepare pure lead hydrogen arsenate, as has been claimed by Morse and Reed.[1]

The preparation of this compound was attempted in several other ways and the best results were obtained by using the following method: Fairly pure lead hydrogen arsenate is prepared by use of the reacton between lead nitrate and di-sodium hydrogen arsenate. The precipitate is washed quite thoroughly with distilled water and then dissolved completely in nitric acid, using just enough of the acid to effect solution. To this solution dilute ammonium hydroxide is added slowly with constant stirring

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[1] *Loc. cit.*

until approximately three-fourths of the nitric acid used has been neutralized. During the addition of the ammonium hydroxide the lead hydrogen arsenate will gradually be precipitated. The precipitate is then allowed to stand over night in contact with the solution (which is acid in reaction due to the presence of considerable amount of nitric acid). The supernatant liquid is then decanted through a filter and the precipitate washed first with distilled water slightly acidulated with nitric acid and then with water which has been recently boiled to remove carbon dioxide, until the washings no longer give a test for nitrates with diphenylamine. The precipitate is then dried at 110°.

The salt obtained in this manner is free from nitrates and ammonium salts. It is pure lead hydrogen arsenate and is a white, amorphous, finely divided, fluffy powder. Analyses made of three samples gave results as follows:

	As as As_2O_5. Per cent.	Pb as PbO. Per cent.	Ratio As_2O_5 to PbO.
Sample No. 1	32.99	63.92	1 : 1.937
Sample No. 2	32.98	63.92	1 : 1.937
Sample No. 3	32.88	63.70	1 : 1.937
Theoretical for $PbHAsO_4$	33.15	64.46	1 : 1.945

It will be noted that the precentages are somewhat lower than the theoretical for lead hydrogen arsenate. This is due to the presence of a small amount of water that cannot be easily removed. Samples do not lose this water below 200°. Experimental work has not been carried out to the point where the writers are able to state if there is a definite temperature at which this moisture can be removed without changing some of the substance into the form of the pyroarsenate. It will also be noted that the ratio of lead oxide to arsenic oxide is a trifle lower than the theoretical. This is due to the fact that the method for determining lead which is now used by the Association of Official Agricultural Chemists is hardly as accurate as the method used for arsenic; there is a tendency for the results to be slightly low.

(2) Results of Attempts to Prepare Lead Orthoarsenate.

The preparation of this compound was first attempted by the use of the reaction between lead acetate and di-sodium hydrogen arsenate. The results obtained showed that this reaction is easily affected by various conditions such as temperature, concentration, the rate in which the substances are brought together, and the amount of salt used in excess. Evidently, this reaction cannot be used to prepare pure orthoarsenate of lead. The insoluble precipitate obtained from the reaction referred to is really a mixture of two different compounds; this will be brought out in a later portion of this paper.

The preparation of the ortho-compound was further attempted by employing the reaction between ammonium hydroxide and lead hydrogen arsenate as has been suggested by Volck.[1] The ammonium hydroxide used was freed from carbonate by redistillation from barium hydroxide. It was found that the reaction between ammonium hydroxide and lead hydrogen arsenate is complete after the mixture had been heated gently on a steam bath for three hours and that the reaction is the same whether only a slight or large excess of ammonium hydroxide is used. Four samples of the substance obtained in this manner were carefully washed free from soluble salts and then dried at 110°. The analyses of the samples are as follows:

	Arsenic as As_2O_5. Per cent.	Lead as PbO. Per cent.	Ratio As_2O_5 to PbO.
Sample No. 1	23.42	74.72	1 : 3.190
Sample No. 2	23.43	74.68	1 : 3.189
Sample No. 3	23.42	74.86	1 : 3.196
Sample No. 4	23.46	74.61	1 : 3.180
Theoretical for $Pb_3(AsO_4)_2$	25.57	74.43	1 : 2.911

These results show that the substance obtained is not a pure orthoarsenate of lead. It contains more lead and less arsenic than the theoretical figures. At first, the authors thought that perhaps there was a small amount of free lead hydroxide present. To ascertain if this were true, the substance was heated in a drying oven to a temperature somewhat greater than 130°. There was no change in color due to the formation of lead oxide nor was there any loss in weight. Even microscopic examination failed to show the presence of any lead oxide. A sample of freshly prepared lead hydroxide, when heated to a temperature a little above 130°, gradually changed to an orange-yellow color with the formation of lead oxide and there was a gradual decrease in weight from loss of water. These results clearly indicate that there is no uncombined lead hydroxide present in the insoluble material resulting from the reaction of ammonium hydroxide with lead hydrogen arsenate. In fact, the tests which have been tried *show that it is a definite chemical compound, a new basic lead arsenate of which there is no mention in the literature.* The analyses indicate that its composition may be represented closely by the formula $21Pb_3(AsO_4)_2.2Pb(OH)_2.10H_2O$. It is a white, amorphous granular powder; microscopical examination does not show any crystalline structure. There is no loss of water at temperatures below 200°.

A number of attempts have been made to prepare a pure orthoarsenate of lead. In these experiments all of the reactions which are now used in the manufacture of lead arsenate have been tried in aqueous solution and also in non-aqueous solutions so far as conditions would permit. Other possible reactions have been investigated. Without going into any lengthy discussion of the reactions used, the authors

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[1] *Loc. cit.*

will state that lead orthoarsenate is not formed under the ordinary aqueous conditions employed in the manufacture of commercial lead arsenate, and that it is not a component of the commercial material as has been formerly supposed. The compound present, which has been represented to be the orthoarsenate, is in reality the basic lead arsenate mentioned above. Further proof of this will be brought out in a later portion of this paper.

(3) The Preparation of Lead Pyroarsenate.

Since the presence of this substance in the ordinary commercial salts used for insecticidal purposes has been suggested, it was deemed advisable to undertake the preparation of the pure compound. It would seem, on theoretical grounds, that the simplest method would be by the removal of water by means of heat from lead hydrogen arsenate.

$$2PbHAsO_4 \longrightarrow Pb_2As_2O_7 + H_2O.$$

Samples of lead hydrogen arsenate were heated in a drying oven to a temperature somewhat higher than 200° without loss in weight. When this compound is fused at a dull red heat, however, it loses water and a white, glassy, somewhat crystalline substance is left on cooling. Analyses made of this substance show it to be the pyroarsenate.

It is well known that pyroarsenic acid does not exist in the presence of water, and consequently if lead pyroarsenate is a constituent of the ordinary commercial salts it must be due to the easy dehydration of lead hydrogen arsenate. The results given above show that this substance has to be heated to a fairly high temperature before loss of water occurs and, evidently, lead pyroarsenate is not a constituent of the commercial lead arsenate.

(4) Specific Gravity and Solubility of Lead Hydrogen Arsenate and Basic Lead Arsenate.

These properties are of much more importance in the consideration of the adaptability of arsenic containing compounds for use as insecticides. A very small amount of soluble arsenic compound is sufficient to cause injury to the foliage of fruit trees. Further, an insecticide should be in a fine state of sub-division and of a specific gravity sufficiently low that it will remain in suspension in water for some length of time.

The specific gravity of lead hydrogen arsenate and basic lead arsenate, as prepared by the above described methods, was found by determining the weight of toluene displaced by a known quantity of the salt. The toluene was first dried by means of solid sodium hydroxide and then distilled. Its specific gravity at 20° referred to water at 4° was found to be 0.8669. Care was taken to remove air from the arsenate when covered with toluene by placing the pycnometer in an exhausted desiccator.

(*a*) LEAD HYDROGEN ARSENATE.

Grams $PbHAsO_4$.	Grams toluene displaced.	Specific gravity $PbHAsO_4$ 20°/4°.
11.1070	1.6610	5.79
11.5724	1.6630	5.79
11.3230	1.6968	5.78
		Average 5.786

(*b*) BASIC LEAD ARSENATE.

Grams basic lead arsenate.	Grams toluene displaced.	Specific gravity basic lead arsenate 20°/4°.
14.5770	1.7794	7.10
20.5749	2.5083	7.11
		Average 7.105

There are several things to be considered in making a determination of the solubility of lead hydrogen arsenate. Although one of the hydrogens of arsenic acid resembles the hydrogen of strong acids in its dissociating tendency, the other two hydrogens are those of weak acids. Hence perceptible hydrolysis takes place in solutions of this acid, even when the base combined is strong; that of tertiary salts being greatest in extent. It is difficult to predict the influence of this hydrolysis upon lead hydrogen arsenate. There is also the possibility of the formation of more insoluble normal or basic salts. In discussing the solubility of lead hydrogen arsenate Volck[1] states that "the liberation of the arsenic oxide (arsenic acid) from the acid arsenates depends on transposition to the ortho or neutral arsenate under neutral or alkaline conditions." He also infers that a given quantity of lead hydrogen arsenate can be completely changed to the orthoarsenate by bringing it in contact with water and then replacing the supernatent liquid from time to time with fresh water.

The writers have endeavored to verify Volck's statements. The experiments tried, however, show that arsenic acid is not formed in sufficient quantity by hydrolysis at room temperature to give the qualitative tests suggested by Volck nor can the composition of lead hydrogen arsenate be changed to any appreciable extent by bringing it in contact with an excess of pure water and removing the supernatant liquid from time to time, even though the operation be continued for several days. At temperatures near the boiling point there is evidence of only a slight hydrolysis. We feel safe in stating that if there is any hydrolysis of this substance it is slight and can only be determined by the use of refined physico-chemical methods.

Unfortunately, other pressing work in progress in this laboratory has prevented the taking up of a critical study of this hydrolysis. An idea of the solubility of the salt was obtained, however, by determining the

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[1] *Loc. cit.*

amount of arsenic in solution when using the provisional method of the Association of Official Agricultural Chemists[1] for the determination of "water-soluble arsenic oxide" in commercial lead arsenate. Eight hundred cc. of the water extract obtained did not contain sufficient arsenic in solution to be quantitatively estimated by making the final titration with 0.02 *N* iodine solution. This result indicates that lead hydrogen arsenate is a very insoluble substance.

In attempting to make a determination of the solubility of basic lead arsenate one meets with the numerous perplexing difficulties which are common with the basic salts. These difficulties are such as to preclude perhaps the securing of quantitative data by the usual methods. Use was made of the method of the Association of Official Agricultural Chemists referred to in the preceding paragraph for getting an idea of the solubility of this substance. There was not sufficient arsenic present in eight hundred cc. of the water extract to be estimated by titration with 0.02 *N* iodine. When warm water was used there was no difference in the results obtained. Evidently, this salt is also very insoluble.

(5) The Quantitative Determination of Lead Hydrogen Arsenate in the Presence of the Basic Arsenate.

At the present time there is no method for estimating the amount of lead hydrogen arsenate in commercial arsenate of lead. It was with the object of securing such a method that this phase of the work was undertaken. It has been shown that when lead hydrogen arsenate is treated with ammonium hydroxide (free from CO_2) under ordinary conditions a basic arsenate of lead of constant composition is formed. The amount of arsenic passing into solution from a given quantity of lead hydrogen arsenate has also been found to be constant. Since the basic arsenate may be considered as insoluble from the usual analytical standpoint, lead hydrogen arsenate in mixtures with the basic arsenate can be easily determined by the following described method:

Take a convenient amount of the finely powdered sample (3–10 g.), depending upon the amount of the acid salt present, which has been dried at 100°, and add 200 cc. of a 5% solution of carbon dioxide-free ammonium hydroxide. Allow to digest with occasional shaking for a few hours at room temperature, when the reaction should be complete. The supernatant liquid is then filtered by suction from the insoluble basic salt by using a Buchner funnel prepared with a pad made of two sheets of filter paper with a layer of asbestos between. The upper paper should be a hardened filter. The filter is finally washed thoroughly with recently boiled distilled water until free from soluble salts. The final washings may be tested with lead nitrate solution to ascertain the completeness of

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[1] *Bull.* 107 (Revised), Bur. of Chem., U. S. Dept. Agr.

the removal of the ammonium arsenate. The filtrate should be perfectly clear. In case there is difficulty in obtaining a clear solution it may be overcome by refiltering through a Gooch crucible having a thin layer of carbon black on an asbestos pad. The final filtrate obtained is made up to convenient volume and an aliquot taken for the determination of arsenic. After free ammonium hydroxide is removed by boiling, the arsenic is determined by the modified Gooch and Browning method.[1] The amount of arsenic in the total filtrate calculated as As_2O_5 and then multiplied by the factor 7.6034 gives the amount of lead hydrogen arsenate present in the original mixture.

This method has been tried out on a number of mixtures of known composition and in each case has given good results.

The nature of the insoluble salts formed by the reaction of lead acetate and lead nitrate with di-sodium hydrogen arsenate has been studied in a limited way by using the above described method in conjunction with the usual analytical methods employed. The results obtained are given in Table I:

TABLE I.—THE COMPOSITION OF PRECIPITATES OBTAINED BY REACTIONS OF LEAD ACETATE AND LEAD NITRATE WITH DI-SODIUM HYDROGEN ARSENATE.

Material.	Total lead as PbO. Per cent.	Total arsenic as As_2O_5. Per cent.	Total $PbHAsO_4$. Per cent.	Ratio of As_2O_5 other than that combined as $PbHAsO_4$ to PbO other than that combined as $PbHAsO_4$.
1. Sample prepared by using $Pb(C_2H_3O_2)_2$ and Na_2HAsO_4 in the theoretical proportion suggested by Haywood	73.21	24.93	14.96	1 : 3.189
2. Sample prepared using Na_2HAsO_4 with $Pb(C_2H_3O_2)_2$ in excess	74.10	24.28	7.42	1 : 3.179
3. Sample made using $Pb(C_2H_3O_2)_2$ with Na_2HAsO_4 in excess	72.96	24.72	10.48	1 : 3.12
4. Sample made using Na_2HAsO_4 with $Pb(NO_3)_2$ in excess	64.73	32.26	93.16	1 : 3.30

These results show that the precipitates obtained were, in each instance, mixtures containing various amounts of the acid salt. It will be noted also that the ratio of the As_2O_5, other than that combined as $PbHAsO_4$, to the PbO, other than that combined as $PbHAsO_4$, approximates within experimental error that found in the basic arsenate already described. These results, considered with the work which has already been presented, seem to leave little doubt that the substance present other than lead hydrogen arsenate is the basic arsenate of lead.

The application of the work here presented to the valuation of commercial samples of lead arsenate will be presented at an early date for publication in the *Journal of Industrial and Engineering Chemistry.*

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[1] *Bull.* 107 (Revised), Bur. of Chem., U. S. Dept. Agr.

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.

CORVALLIS, OREGON.

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

THORIUM AMMONIUM OXALATE.

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

Received June 4, 1914.

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.