Summary.

It has been shown that basic mixtures, and not chemical compounds, are obtained by the addition of soluble vanadates to solutions of beryllium salts.

A new compound, beryllium metavanadate tetrahydrate, has been prepared, and its properties described.

TUCSON, ARIZ.

THE ARSENATES OF LEAD.

[SECOND PAPER.]

EQUILIBRIUM IN THE SYSTEM PbO, As_2O_5, H_2O.

BY C. C. McDONNELL AND C. M. SMITH.

Received October 4, 1916.

In a preceding article[1] we showed that trilead arsenate, although spoken of freely in the literature, is not so easily produced as is ordinarily believed. Double decomposition between soluble lead salts and soluble arsenates rarely gives a product of theoretical composition, and the action of excess ammonia on dilead arsenate leads to the formation of a basic compound, as was first recorded by Tartar and Robinson.[2] These facts suggested that trilead arsenate is relatively unstable and capable of existing only under very limited conditions. In order to clear up this point the following phase rule study was undertaken.

The three component system PbO, As_2O_5 and H_2O can easily be investigated as far as mono- and dilead arsenates are concerned, but the system as such cannot be followed beyond dilead arsenate, owing to the insolubility of lead hydroxide. This necessitates the use of some other base to produce alkalinity. Ammonia seemed particularly suitable for this purpose, since it is easily prepared free from carbon dioxide, has practically no solvent action on lead compounds, and does not form double salts under conditions such as obtained in these experiments. Then, too, it is of especial interest since its action on dilead arsenate has long been considered the best means of producing trilead arsenate, as first stated by Berzelius.[3]

The use of ammonia in such a system introduces a fourth component, but by keeping its concentration constant one degree of freedom is destroyed, and the system will behave like a three-component one. (Owing to the low concentrations employed, we are justified in the assumption that the volume changes were nil or insignificant.)

The experiments were carried out in the following manner: Pure ammonia water was prepared (by distilling concentrated C. P. ammonia water over barium hydroxide to remove CO_2, and absorbing the evolved

---

[1] THIS JOURNAL, 38, 2027 (1916).

[2] *Ibid.*, 36, 1848 (1914).

[3] *Ann. chim. phys.*, [2] 11, 229 (1819).

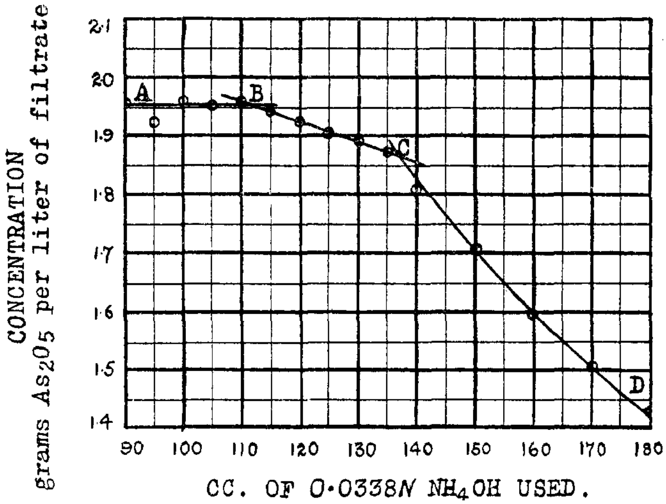
vapors in recently boiled and cooled distilled water) and diluted to 0.0338 *N* (arbitrary dilution). A series of 2 g. portions of pure amorphous dilead arsenate, $PbHAsO_4$, were put into flasks, and to them were added varying amounts, from 90 to 180 cc., of the dilute ammonia solution.

All of the mixtures were put into a shaking machine and agitated for seven hours on each of two successive days at 32° ± 1°. (It was determined that equilibrium had been reached in this time.) After allowing the mixtures to settle, they were filtered on Gooch crucibles containing disks of filter paper and the clear filtrates analyzed. The results showed that only a mere trace of lead went into solution, but a considerable amount of arsenic, indicating that the reaction consisted in the removal of a portion of the arsenic acid from the dilead arsenate to form soluble ammonium arsenate. The course of the reaction could, therefore, be followed by determining the arsenic oxide in solution, the results of which are here tabulated.

Cc. of 0.0338 *N* NH_4OH used.	G. of As_2O_5 per liter of filtrate.	Total g. of As_2O_5 dissolved.
90	1.956	0.1760
95	1.925	0.1829
100	1.960	0.1960
105	1.953	0.2051
110	1.960	0.2156
115	1.941	0.2232
120	1.926	0.2311
125	1.902	0.2378
130	1.891	0.2459
135	1.871	0.2526
140	1.809	0.2533
150	1.706	0.2559
160	1.591	0.2546
170	1.503	0.2555
180	1.429	0.2572

The significance of these results is brought out more clearly in the accompanying graph.

The first additions of ammonia have resulted in the formation of a constant solution, as shown by the branch A–B of the graph, which, in a three-component system at constant temperature, indicates the existence of two solid phases. One of these must, of course, be the unchanged dilead arsenate, and the other may easily be determined as follows: The constant solution contains 1.951 g. As_2O_5 per liter, and the break B in the graph occurs at 112 cc., making the total dissolved As_2O_5 = 0.2185 g. The transposition of 2 g. of dilead arsenate to trilead arsenate requires the solution of 0.2208 g. As_2O_5. The molecular ratio of the residue, PbO/As_2O_5, figures out as 2.99, showing that trilead arsenate is the second solid phase. Analysis of the residues immediately preceding and following the point B gave 25.65 and 25.31% As_2O_5, respectively, while the formula $Pb_3(AsO_4)_2$ requires 25.56%, which is additional confirmation that it is trilead arsenate. The constant solution (to the point B) contains 0.00849 mol. As_2O_5 per liter, making the molecular ratio $NH_4OH/As_2O_5 = 3.98$, which is practically equivalent to a solution of diammonium hydrogen arsenate, $(NH_4)_2HAsO_4$.



The portion B–C of the graph shows why trilead arsenate is not ordinarily obtained by double decomposition. If, after all the dilead arsenate was changed to the tri-salt, the latter remained as such on adding more ammonia, the total dissolved As_2O_5 would remain constant and the graph become a rectangular hyperbola. But a continued increase is shown in the total As_2O_5 dissolved and the branch B–C is a straight line. This indicates the formation of a series of solid solutions, with trilead arsenate as one end member and some basic arsenate as the other. At the point C 0.2553 g. of As_2O_5 has been dissolved, leaving in the residue 0.407 g. As_2O_5 and 1.286 g. PbO, giving a molecular ratio $PbO/As_2O_5 = 3.253$.

Beyond the point C, the total dissolved As_2O_5 remains practically constant, and the graph then becomes a rectangular hyperbola, showing that this basic arsenate is not further changed within the limits of our experiments. A large excess of ammonia water produces a product only slightly more basic, having a molecular ratio about 3.30.

About 100 g. of trilead arsenate were prepared by treating dilead arsenate with the theoretical amount of $N/10$ ammonia, as calculated from the foregoing data. Analysis:

	Dried at 110°.	Anhydrous.	Theory for $Pb_3(AsO_4)_2$.
Lead oxide, PbO	73.62%	74.30%	74.44%
Arsenic oxide, As_2O_5	25.46%	25.70%	25.56%
Water (by ignition)	0.92%	.....	.....
	100.00%	100.00%	100.00%

The product contains a small amount of water which is not expelled at 110°. This corresponds to slightly less than $^1/_2$ molecule. It is an amorphous powder, with a specific gravity, 15/4 of 7.00. Crystallized trilead arsenate (anhydrous) prepared by fusion, had a specific gravity 15/4 of 7.30.

Summary.

It has been shown that the action of dilute ammonia on dilead orthoarsenate proceeds as follows:

(1) Transposition to trilead orthoarsenate, $Pb_3(AsO_4)_2$, the supernatant solution remaining constant at the $(NH_4)_2HAsO_4$ stage until transformation is complete.

(2) Formation of solid solutions ranging from trilead arsenate to a basic arsenate, beyond which no further change occurs.

Insecticide and Fungicide Laboratory,
Miscellaneous Division, Bureau of Chemistry.
Washington, D. C.

[Contribution from the School of Chemistry of the University of Virginia.]

THE REDUCTION OF VANADIC ACID BY HYDRIODIC ACID.

By Graham Edgar.

Received August 28, 1916.

In a recent paper by Ditz and Bardach[1] experimental results are given which indicate that the reduction of vanadic acid by hydriodic acid at room temperature and at considerable dilution proceeds irregularly, and that the iodine liberated in the course of the reaction corresponds approximately to that calculated for the reaction

$$V_2O_5 + 4HI \longrightarrow V_2O_3 + 2H_2O,$$

or in some instances to an even greater amount. At the same time it is pointed out that tetravalent vanadium is relatively stable towards dilute hydriodic acid. In order to explain their results, Ditz and Bardach offer the hypothesis that the reduction of vanadic acid by hydriodic acid proceeds directly from the pentavalent to the trivalent state, without the formation of tetravalent vanadium as an intermediate product.

The results of Ditz and Bardach conflict with those of several earlier investigators. Numerous statements occur in the literature to the effect that reduction of vanadic acid by dilute hydriodic acid proceeds until the vanadium approximates the *tetravalent* condition,[2] and several investigators have defined conditions under which a quantitative reduction may be expected, and have based methods for the estimation of vanadium

---

[1] *Z. anorg. Chem.*, **93**, 97 (1915).

[2] Browning, *Am. J. Sci.*, [4] **2**, 185 (1896); Hett and Gilbert, *Z. öffentl. Chem.*, **12**, 265 (1906); Warynski and Mdivani, *Mon. Sci.*, **22**, II, 527 (1908); Perkins, *Am. J. Sci.*, [4] **29**, 540; Rosenheim, *Inaug. Diss. Berlin* (1888).