

approximately in the molar ratio of 6 SnO<sub>2</sub> to 1 Cr<sub>2</sub>O<sub>3</sub>, may be obtained by adding an equivalent amount of dichromate solution to stannous chloride and dialyzing the mixture. The hydrosol will contain all of the tin and practically one-half of the chromium used in the reaction.

4. The equations for the reaction have been formulated.

5. The work already completed as well as that now in progress on oxidation and reduction without the addition of acid justifies the conclusion that colloidal hydrous oxides are obtained in an oxidation-reduction reaction, in which acid must be added for the formation of normal salts, if the stoichiometric relations are the same with and without acid.

PITTSBURG, PA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY.]

## THE ACTION OF HYDROGEN SULFIDE ON ARSENIC ACID.

By WILLIAM FOSTER.

Received August 9, 1915.

### I. Introduction.

Sometime ago my colleague, Professor LeRoy W. McCay, called my attention to a paper published by Usher and Travers<sup>1</sup> in 1905, and entitled "The Interaction of Sulfuretted Hydrogen and Arsenic Pentoxide in Presence of Hydrochloric Acid." Inasmuch as this paper contained some statements apparently not in harmony with the results obtained by McCay years before, it seemed well worth while to conduct experiments with the view of accounting for the discrepancies existing between the authors.

Ever since the days of Berzelius there has been a difference of opinion as to the chemical changes that occur when solutions of arsenic acid or acidulated solutions of arseniates are treated with hydrogen sulfide.<sup>2</sup>

Usher and Travers repeated and confirmed Brauner and Tomicek's work in the case of dilute hydrochloric acid solutions of arsenic acid, and also extended the investigation to solutions containing up to 32% of HCl, and obtained the results given below. The experiments were carried out at about 15°, and in every case the solution contained 0.3664% of the pentoxide.

<sup>1</sup> *Trans.*, 87, 1370 (1905).

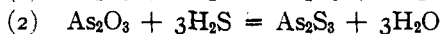
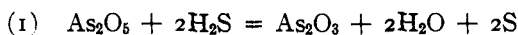
<sup>2</sup> For detailed information, the reader is referred to the following literature on the subject: Berzelius, *Ann. der Phys. u. Chem.*, 7, 2 (1826); H. Rose, *Ibid.*, 107, 186 (1859); Wackenroder, "Dictate of Forensic Chemistry," H. Ludwig, *Archiv. der Phar.*, 2 te Reihe, 97, 32; Fuchs, *Z. anal. Chem.*, 1, 189 (1862); Bunsen, *Ann. Chem.*, 192, 305 (1878); McCay, *Am. Chem. J.*, 9, 174 (1887); *Chem. News*, 54, 287 (1886); *Am. Chem. J.*, 10, 6 (1888); *Z. anal. Chem.*, 27, 632 (1888); *Z. anorg. Chem.*, 29, 36 (1901); Brauner and Tomicek, *Trans.*, 53, 145 (1888); *Neher. Z. anal. Chem.*, 32, 45 (1893).

| HCl. %. | Comp. of ppt.                                 | HCl. %. | Comp. of ppt.                                 |
|---------|---|---------|---|
| 1.8     | As <sub>2</sub> S <sub>5</sub> , 91 per cent. | 14.34   | As <sub>2</sub> S <sub>5</sub> , pure         |
| 7.9     | As <sub>2</sub> S <sub>5</sub> , pure         | 25.10   | As <sub>2</sub> S <sub>5</sub> , 58 per cent. |
| 10.76   | As <sub>2</sub> S <sub>5</sub> , pure         | 32.27   | As <sub>2</sub> S <sub>5</sub> , pure         |

The authors also add: "The solution was contained in a flask, and sulfuretted hydrogen was slowly bubbled through the liquid at the rate of five bubbles per second. After about twelve hours, the current of gas was stopped, and the precipitate was collected, etc."

The surprising thing is, that Usher and Travers should have obtained only 91% of As<sub>2</sub>S<sub>5</sub> in the most dilute hydrochloric acid used (1.8%), pure As<sub>2</sub>S<sub>5</sub> in acid concentrations ranging from 7.9 to 14.34% of hydrochloric acid, and then, in stronger acid solutions, less and less pentasulfide with a corresponding increase in trisulfide.

The authors also say that the reaction between arsenic acid and hydrogen sulfide, in the presence of small concentration of hydrochloric acid, may be supposed to take place as follows:



This is the old hypothesis of Rose, and it is not in harmony with the facts.

## II. Experimental.

As the result of numerous experiments the author arrived at the following conclusions:

(a) The writer agrees with McCay in the observation that arsenic acid is never reduced by hydrogen sulfide directly to arsenious acid and free sulfur according to the old hypothesis of Rose, which is still found in many text-books on chemistry.<sup>1</sup>

(b) When a solution of arsenic acid is treated with hydrogen sulfide the compounds first interact to form monosulfoxyarsenic acid (H<sub>3</sub>AsO<sub>3</sub>S) as held by McCay. H<sub>3</sub>AsO<sub>3</sub>S is somewhat unstable. In the presence of dilute acids, it breaks down gradually into arsenious acid and sulfur; in the presence of high concentrations of acids, it is much more unstable. Concentrated hydrochloric acid brings about the decomposition *very quickly*, even at 0°. A low concentration of hydrogen sulfide also favors the breaking down of the compound. This fact, and not the hypothesis of Rose, accounts for the presence of As<sub>2</sub>S<sub>3</sub> and free sulfur frequently observed in precipitates obtained by treating arsenic acid with hydrogen sulfide.

<sup>1</sup> The quantitative method for the determination of arsenic as the trisulfide in "Quantitative Chemical Analysis," by Fresenius-Cohn, Vol. I, pp. 415-416 (1904) is open to serious criticism on the ground that when a solution of arsenic acid is treated with hydrogen sulfide under *ordinary conditions* the precipitate is not pure arsenic trisulfide. Arsenic pentasulfide is always present in the precipitate.

(c) When solutions of arsenic acid are treated with a *rapid* stream of hydrogen sulfide no reduction takes place, even if no mineral acid be present. It was observed that *arsenic acid saturated with hydrogen sulfide yielded pure arsenic pentasulfide after the solution had stood for ninety-one hours*. It was also observed that no reduction occurred in solutions of arsenic acid in the presence of hydrochloric acid ranging in concentration from 0.9% to 32%, *i. e.*, when the solutions were treated at 15° with a *rapid* stream of hydrogen sulfide.

(d) The results of all the experiments carried out are in complete harmony with all the results formerly obtained by McCay. On the other hand, however, very few of the results agree with those obtained by Usher and Travers.<sup>1</sup>

The conclusions summarized above are based upon the following experiments which were selected as representative of a much larger number carried out:

**A. Qualitative Experiments.**—(1) According to Usher and Travers, hydrogen sulfide has a marked reducing action on arsenic acid containing 1.8% of hydrochloric acid, for they obtained from such a solution a low yield (91%) of arsenic pentasulfide. To test this conclusion, a solution of arsenic acid and hydrochloric acid was prepared having approximately the strength of the solution analyzed by Usher and Travers. A little over 100 cc. of this solution were treated with 10 cc. of hydrogen sulfide water 0.0206 g. (H<sub>2</sub>S), and allowed to stand at about 15°. Even at the end of five hours not the least turbidity was present, thus indicating that no reduction had taken place. The H<sub>2</sub>S interacted with H<sub>3</sub>AsO<sub>4</sub> to form H<sub>3</sub>AsO<sub>3</sub>S. The presence of H<sub>3</sub>AsO<sub>3</sub>S and the absence of H<sub>2</sub>S were proved by the tests employed by McCay.<sup>2</sup> This experiment was confirmed *quantitatively* as will be shown below.

(2) A solution of H<sub>3</sub>AsO<sub>4</sub> containing one volume of water to one of concentrated hydrochloric acid was treated with a *few bubbles* of H<sub>2</sub>S, whereupon sulfur (white) separated out very quickly. On removing the free sulfur and any possible H<sub>2</sub>S that might be present and heating the clear filtrate, more sulfur separated out. The same result was obtained in the presence of two volumes of conc. hydrochloric acid to one of water. When solutions of Na<sub>3</sub>AsO<sub>3</sub>S.12H<sub>2</sub>O containing the same concentrations of acid were prepared, the free sulfur removed, and the clear filtrates boiled, sulfur separated out as before.

When H<sub>3</sub>AsO<sub>4</sub> was dissolved in conc. hydrochloric acid, the solution cooled to 0° and a little H<sub>2</sub>S passed in, sulfur separated out; but on boiling the solution after the removal of free sulfur, no more sulfur separated out. The same result was also obtained at —20°. When Na<sub>3</sub>AsO<sub>3</sub>S.12H<sub>2</sub>O

<sup>1</sup> *Trans.*, 87, 1370 (1905).

<sup>2</sup> *Am. Chem. J.*, 10, 6, 4 (1888).

was dissolved in conc. hydrochloric acid at  $0^{\circ}$  and  $-20^{\circ}$ , respectively, the free sulfur removed, and the clear solutions boiled, no sulfur separated out.

These experiments show that  $H_3AsO_4$  and  $H_2S$  first interact to form  $H_3AsO_3S$ , but that heat and strong hydrochloric acid break down the latter substance with the separation of sulfur. The decomposition is brought about very quickly by concentrated hydrochloric acid, even at low temperature, but the separation of sulfur is retarded in case the acid is more dilute.

**B. Quantitative Experiments.**—For the purpose of verifying some of the results obtained by Usher and Travers, a large number of quantitative determinations of the arsenic in solutions of arsenic acid was next made under different conditions. With this end in view, about a liter of an aqueous solution of arsenic acid was prepared, and it was found by careful analysis that 10 cc. of the solution at  $25^{\circ}$  contained 0.1751 g.  $As_2O_5$ , which corresponds to 0.2363 g. of  $As_2S_5$ . Portions of 10 cc. of this solution were used in the determinations described below. By properly diluting the portion measured out, a solution was obtained in each case containing approximately 0.3664% of  $As_2O_5$ , the strength of the solution analyzed by Usher and Travers.

The arsenic in the various solutions was determined by McCay's method, *i. e.*, by heating the solutions of  $H_3AsO_4$  and  $H_2S$  in heavy glass bottles having ground glass stoppers. The sulfide of arsenic was collected in Gooch crucibles, washed with water, followed by alcohol and carbon bisulfide to remove any free sulfur, and then dried at  $110^{\circ}$ .

(1) A rapid stream of  $H_2S$  was passed to opalescence into two portions of the solution of  $H_3AsO_4$  containing 1.8% of HCl, followed by heating under pressure in a water bath. The following results were obtained:

Wt. of  $As_2S_5$ : (a) 0.2363 g. (b) 0.2362 g.

As the yield of  $As_2S_5$  was quantitative, no reduction had taken place. Almost identical results were obtained in the presence of 0.9% of HCl.

Solutions of arsenic acid containing 1.8% of HCl were introduced into two bottles, the latter joined in tandem, and  $H_2S$  passed at the rate of about one bubble a second for 31 hours; the bottles were then stoppered and allowed to stand at room temperature for about two days. The arsenic acid was then determined as usual.

Weight of precipitate: (a) 0.2352 g. (b) 0.2347 g.

The results are a little low, due to the decomposition of a small amount of the  $H_3AsO_3S$ . This conclusion was confirmed by tests made on  $Na_3AsO_3S \cdot 12H_2O$ , *i. e.*, it was proved that hydrochloric acid 1.8% in strength slowly splits off sulfur from  $H_3AsO_3S$ .

(2) In this experiment the  $H_2S$  was passed through the solutions under the conditions given by Usher and Travers.

After the gas had been passed through for twelve hours, the bottles were stoppered and allowed to stand for another twelve hours and then the determination of arsenic made as usual.

Weight of sulfide found: (a) 0.2370 g. (b) 0.2363 g.

The alcohol-carbon bisulfide liquid obtained by washing the precipitates were evaporated to dryness, and a negligible residue was obtained. I fail to see why Usher and Travers obtained only 91% of  $\text{As}_2\text{S}_5$  when working under practically the same conditions.

(3) Two portions of the solution of  $\text{H}_3\text{AsO}_4$  containing no HCl were treated to saturation with a *rapid* stream of  $\text{H}_2\text{S}$ , the bottles stoppered and allowed to stand for ninety-one hours. At the end of this period 10 cc. of conc. HCl were added to the contents of each bottle, and the arsenic determined as before.

Wt. of precipitate: (a) 0.2360 g. (b) 0.2363 g.

The conclusion is definite, therefore, that *an excess of  $\text{H}_2\text{S}$  will not reduce  $\text{H}_3\text{AsO}_4$ , even in the course of four days.*

(4) A solution of  $\text{H}_3\text{AsO}_4$  containing 25% of HCl was treated to saturation with a *rapid* stream of  $\text{H}_2\text{S}$ . The weight of precipitate ( $\text{As}_2\text{S}_5$ ) obtained was 0.2364 g.—a quantitative yield. This agrees with the observation made by Neher.

Two solutions of arsenic acid were prepared containing 25% of HCl, the bottles joined in tandem, and a current of  $\text{H}_2\text{S}$  passed through at the rate of about five bubbles a second for a period of twelve hours. At the start, the first solution dissolved, of course, almost the entire amount of  $\text{H}_2\text{S}$  passing, so in the first bottle a precipitate of sulfide of arsenic made its appearance in about a minute, and in the course of five minutes a fair amount of precipitate had formed. A precipitate appeared in the second bottle in about five minutes. After the gas had passed through the solutions for twelve hours, the bottles were stoppered for another twelve hours, and the precipitate treated in the usual way.

Weights of precipitate: (a) 0.2367 g. (quantitative). (b) 0.2283 g. (8 mg. low).

There was no reduction in the case of (a), but in (b) there was a loss of considerable sulfur.

The alcohol-carbon bisulfide mixtures used in washing the precipitates were evaporated to dryness to recover any sulfur which might be in solution. In the first case the residue was negligible, while in the second case it was considerable. This was anticipated, and the explanation is clearly evident in view of all that has been said. In the second solution  $\text{H}_2\text{S}$  was received at a slower rate, and the concentration of the gas was so low, especially at the beginning of the experiment, that the  $\text{H}_3\text{AsO}_3\text{S}$  which was first formed was soon decomposed into  $\text{H}_3\text{AsO}_3$  and sulfur, due to the high concentration of the hydrochloric acid.

<sup>1</sup> *Z. anal. Chem.*, 32, 45 (1893).

(5) Two solutions of arsenic acid containing 32% of HCl were treated a few minutes with a *rapid* stream of H<sub>2</sub>S, and the determination of arsenic carried out as usual.

Weights of arsenic sulfide: (a) 0.2367 g. (b) 0.2369 g.

Again there was no reduction of arsenic acid, for the yield of As<sub>2</sub>S<sub>3</sub> was quantitative.

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## A THEORY OF MULTIPLE IONIZATION: A MODIFICATION OF THE ELECTROLYTIC DISSOCIATION THEORY.

### I. INTRODUCTORY AND QUALITATIVE STATEMENT OF THE THEORY, WITH APPLICATIONS.<sup>1</sup>

BY FRANCIS FARNHAM HEYROTH.

Received October 29, 1915.

In the extended application of the electrolytic dissociation theory to general and analytical chemistry which has been made and has been embodied in many textbooks, certain difficulties have been encountered. These have been satisfactorily met by making assumptions at variance with the original propositions of the theory. As such assumptions as have, from time to time, been proposed are widely scattered throughout the literature and are only occasionally alluded to in the textbooks, it seems that a comprehensive theory should be developed to embody the new conceptions as well as to show their relation to the original hypothesis.

The phenomena which the ionic theory, as it is most widely understood, fails to explain, or in regard to which further explanation is to be desired, will now be enumerated under five classes, and then a modification of the theory will be suggested which, it is hoped, will sufficiently explain most of the hitherto obscure facts.

1. We should like to have some insight into the cause of the different degrees of ionization of electrolytes. Why is one acid strong and another weak? The ionic theory offers no hypothesis to explain this.

2. There are certain types of reactions and certain compounds that seem to find no place in the theory. Such compounds are nitrosyl chloride, sulfuryl chloride, phosgene, nitrogen chloride, compounds of the halogens with each other, and practically all acid anhydrides. Nitrogen tetroxide dissolves in water to form a mixture of acids. In all the reactions of these compounds with water ionogens are formed. Are they not formed by ionic actions? Abegg<sup>2</sup> says:

<sup>1</sup> This paper, read before the Cincinnati Section on May 12, 1915, forms the basis of a thesis submitted to the Ohio Mechanics Institute for the Degree of Bachelor of Science.

<sup>2</sup> Abegg, "The Theory of Electrolytic Dissociation," 1907, p. 161.