

article, all of which are based on absolute measurements,<sup>4</sup> and which give a value,  $\mu = 3.90 \times 10^{-18}$  e.s.u., for nitrobenzene in benzene solution. On this basis the results for *o*-dinitrobenzene and the nitrotoluenes must be virtually in agreement. In the case of the *p*-dinitrobenzene inaccuracies in the method of calculation which has to be employed will probably account for the high electric moment,  $\mu = 0.80 \times 10^{-18}$  e.s.u., obtained by Höjendahl. Its value should approach zero.

The value obtained for *m*-dinitrobenzene, on the basis of the reasoning given above, is not in agreement with that reported in this article.

Højendahl<sup>10</sup> has more recently repeated the measurements on the system benzene-*m*-dinitrobenzene, giving a value  $\mu = 3.70 \times 10^{-18}$  for *m*-dinitrobenzene, one which is substantially in agreement with that presented in this article.

### Summary

1. Dielectric constant and density data at 25° have been obtained for benzene solutions of nitrobenzene, *o*-, *m*- and *p*-dinitrobenzene, symmetrical trinitrobenzene and *o*-, *m*- and *p*-nitrotoluene.

2. The data have been applied to the calculations of the electric moments of the various solute molecules.

3. The results of these calculations have been critically discussed. In a number of cases they have been compared with the results of other investigators. They are in agreement with the physical basis provided by Errera, Smyth and Morgan, Thomson, and others, for the determination of the positive or negative character of the benzene substituents.

MADISON, WISCONSIN

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[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, PRINCETON UNIVERSITY]

## A NEW METHOD FOR SEPARATING ARSENIC FROM ANTIMONY

BY LEROY W. MCCAY

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### Introduction

The conversion of arsenic into arsenic acid according to Reich and Richter,<sup>1</sup> its precipitation as silver arsenate and the calculation of the arsenic from the weight of the salt, or the amount of silver in it, have been studied by Pearce and Low,<sup>2</sup> McCay<sup>3</sup> and, comparatively recently, by Eschweiler and Röhrs.<sup>4</sup>

<sup>1</sup> Post, "Chemisch-Technische Analyse," Vieweg and Son, Braunschweig, 1881, p. 396; see also Dingler's *Polyt. Journ.*, **50**, 475 (1883).

<sup>2</sup> Pearce and Low, *Chem. News*, **48**, 85 (1883).

<sup>3</sup> McCay, *ibid.*, **48**, 7 (1883); *Am. Chem. J.*, **8**, 77 (1886).

<sup>4</sup> Eschweiler and Röhrs, *Z. angew. Chem.*, **36**, 464 (1923).

When a *hydrofluoric acid* solution of arsenic acid is neutralized with ammonium or potassium hydroxide, and silver nitrate added to it, all of the arsenic is immediately precipitated as silver arsenate.

Antimonic acid and its alkali salts dissolve readily and completely in warm, moderately dilute hydrofluoric acid, and the solutions can be diluted indefinitely with water without becoming turbid. Such solutions yield no precipitates when neutralized or made alkaline with ammonium or potassium hydroxide. A neutral solution of an alkali antimoniate gives with silver nitrate a white, curdy precipitate of silver antimoniate. If, however, the solution be made strongly acid with hydrofluoric acid and then neutralized, the addition to it of silver nitrate forms no precipitate, if the materials and reagents are free from chlorides. The resulting solution is perfectly clear, and remains so permanently. Antimony pentafluoride is an extremely stable compound, so stable, indeed, that its aqueous solution, providing a little free hydrofluoric acid be present, undergoes no change, or a very sluggish one, when treated with hydrogen sulfide,<sup>5</sup> a fact used in testing antimonic acid for trivalent antimony. On the difference in the behavior of neutralized hydrofluoric acid solutions of arsenic and antimonic acids toward silver nitrate I have based a very satisfactory method for separating arsenic from antimony.

### Experimental Part

A solution of dihydrogen potassium arsenate was made up by dissolving 12 g. of the salt in two liters of water, and the arsenic in 25 cc. was determined (1) by the pentasulfide<sup>6</sup> and (2) by the Reich-Richter method (Pearce-Low modification); found according to (1) 0.0631 and 0.0632 g. As, and according to (2) 0.0628 and 0.0630 g. The average of the four results is 0.0630 g. In a sample of crystalline potassium acid pyroantimonate tetrahydrate quite free from arsenic, the antimony was determined by dissolving a convenient amount in a small platinum dish in about 25 cc. of hot dilute nitric acid to which 2-3 cc. of 48% hydrofluoric acid had been added.<sup>7</sup> The solution was transferred to a 400cc. quartz dish, diluted somewhat, 10-15 cc. of concd. sulfuric acid was added to it, the liquid was evaporated as far as possible on the water-bath and then heated carefully<sup>8</sup> for a few minutes to strong fuming over a free flame. To reduce the antimony to the trivalent state, a piece of sulfur weighing

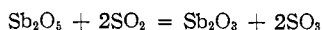
<sup>5</sup> McCay, *THIS JOURNAL*, 31, 374 (1909); Furman, *Ind. Eng. Chem.*, 15, 1073 (1923), footnote.

<sup>6</sup> McCay, *Am. Chem. J.*, 9, 174 (1887).

<sup>7</sup> Nitro-hydrofluoric acid is the best of solvents for tin and antimony and their alloys [McCay, *THIS JOURNAL*, 36, 2375 (1914)].

<sup>8</sup> Just before the acid begins to fume there is a slight effervescence, due probably to the decomposition of the fluorides. Owing to the size of the dish, however, there is little danger of loss.

about 2 g. was now dropped into the dish, it was covered and the acid heated to gentle boiling for twenty minutes. In the main



When cold, 100 cc. of dilute hydrochloric acid (20 cc. concd. HCl to 80 cc. of H<sub>2</sub>O) was poured into the dish, the sulfur was filtered off, the volume of the filtrate brought to 200 cc. and the antimony determined with a 0.1 N KMnO<sub>4</sub> solution (Kessler),<sup>9</sup> or a 0.1 N KBrO<sub>3</sub> solution (Györy).<sup>10</sup> Both solutions were standardized against purest antimony. The average of four closely agreeing results obtained by the former method was 47.95%, the average of two by the latter 47.96%. Of the two methods that of Györy is the more reliable.

Weighed amounts of the pyro salt were dissolved as above directed in a platinum dish holding comfortably 250 cc., known volumes of the standard solution of the potassium arsenate run in, the volume in each case was brought to 100 cc. and the solution neutralized as follows: a drop of methyl orange was added and strong ammonia dropped in until every trace of pink had disappeared; the liquid was of a pure gold color and faintly but distinctly alkaline to sensitive litmus paper. The solution was then heated to boiling and the arsenic precipitated as silver arsenate with silver nitrate in slight excess. After long and vigorous stirring with a platinum spatula, tied to the end of a short stick, so as to coagulate the precipitate and cause it to settle completely, the clear supernatant liquid was tested with a piece of sensitive litmus paper. When not distinctly alkaline, a few drops of dilute ammonia (1 vol. concd. NH<sub>4</sub>OH solution to 4 vols. H<sub>2</sub>O) were added until the paper became decidedly blue and a single drop produced in the clear supernatant liquid no trace of turbidity. No precipitation of silver oxide is possible.<sup>11</sup> This method of neutralizing the solution is more reliable than that of Bennett.<sup>12</sup> His solutions contained no antimony and, of course, no hydrofluoric acid.

Silver arsenate is slightly soluble in water. According to G. S. Whitby,<sup>13</sup> 100 g. of water at 20° dissolves 0.00085 g. of the salt. According to my experiments, 100 g. of water at laboratory temperature dissolves 0.0013 g. (average of four well agreeing determinations). In water containing *silver nitrate*, even when ammonium nitrate or sulfate is present and the solution is decidedly ammoniacal, the solubility of the salt is practically negligible.

When cold, the silver arsenate was transferred to a filter paper, or Neubauer crucible, and washed with water containing ammonium nitrate

<sup>9</sup> As modified by Petriccioli and Reuter, *Z. angew. Chem.*, **14**, 1179 (1901).

<sup>10</sup> Györy, *Z. anal. Chem.*, **32**, 415 (1893).

<sup>11</sup> Wetzlar, "Gmelin-Kraut's Handbuch der anorg. Chemie," 1914, Band V, Abt. 2, p. 68; Low, *Chem. News*, **48**, 85 (1883).

<sup>12</sup> Bennett, *THIS JOURNAL*, **21**, 431 (1899).

<sup>13</sup> Whitby, *Z. anorg. Chem.*, **67**, 107 (1910).

and a little silver nitrate (5. g. of  $\text{NH}_4\text{NO}_3$  and 0.25 g. of  $\text{AgNO}_3$  per liter). The amount of silver nitrate adhering to the well-drained precipitate is so small that it may be disregarded. For safety's sake, however, it may be removed with a little alcohol, the washings being rejected, as they contain no antimony. The precipitate was finally dissolved in nitric acid and the silver determined according to Volhard. The filtrate was caught in a Pyrex flask or beaker and, after the removal of the silver with a minimum amount of hydrochloric acid, poured into the large quartz dish, 10–15 cc. of concd. sulfuric acid was added and the evaporation, reduction and titration were carried out as already directed. Both arsenic and antimony being determined volumetrically, no errors can be caused by the entrance into the solutions of materials dissolved from the glass funnels, flasks, etc.

TABLE I  
SEPARATION OF ARSENIC AND ANTIMONY

| As taken<br>(as $\text{H}_2\text{KAsO}_4$ ),<br>g. | As found,<br>g. | Antimony taken<br>(as $\text{H}_2\text{K}_2\text{Sb}_2\text{O}_7 + 4\text{H}_2\text{O}$ ),<br>g. | Antimony<br>found,<br>g. |
|--|-----------------|--|--------------------------|
| 0.0630   | 0.0630          | 0.1932   | 0.1933                   |
| .0630  | .0629           | .1514  | .1516                    |
| .0630  | .0628           | .1201  | .1205                    |
| .0630  | .0630           | .1105  | .1104                    |
| .0630  | .0631           | .1404  | .1405                    |
| .0252  | .0251           | .0960  | .0958                    |
| .0252  | .0252           | .0965  | .0973                    |

The antimony was determined by titration with potassium permanganate.

While arsenic is converted into its higher state of oxidation with ease, the complete oxidation of antimony to its quinquivalent condition takes place with difficulty.<sup>14</sup> The product left on treating antimony with hot fuming nitric acid in large excess always contains some of the element in the trivalent condition. Concentrated hydrochloric acid and potassium chlorate, permanganic and chromic acids cannot for obvious reasons be employed here. My experience has been that potassium persulfate is the best reagent for effecting a complete oxidation. This fact having been established by a large number of qualitative experiments, 1.983 g. of pure antimony was dissolved in a platinum dish in 50 cc. of hot nitro-hydrofluoric acid, prepared by mixing 40 cc. of dilute nitric acid (1:4) with 5 cc. of 48% hydrofluoric acid. The resulting solution was diluted to about 100 cc., most of the free acid neutralized with ammonia, the liquid heated to gentle boiling and 6 g. of potassium persulfate added in small portions at a time. During the boiling the dish was kept covered with a quartz clock glass. When cold, the solution was neutralized with ammonia and diluted to 500 cc.; found, in 25 cc., 0.0994 g. of

<sup>14</sup> Bošek, *Trans. Chem. Soc.*, 1895, p. 515; Hoffman, *Inaug. Dissert.*, Berlin, 1911.

Sb. By Rose's test<sup>15</sup> not a trace of trivalent antimony could be detected in it. With this standard solution<sup>16</sup> and that of the dihydrogen potassium arsenate used in the first series of separations the results given in Table II were obtained. To the mixture of convenient amounts of the two solutions a few drops of nitric acid and 2-3 cc. of hydrofluoric acid were added and the separations and determinations carried out as above directed.

TABLE II  
SEPARATION OF ARSENIC AND ANTIMONY

| As taken,<br>g. | As found,<br>g. | Sb taken,<br>g. | Sb found,<br>g. |
|-----------------|-----------------|-----------------|-----------------|
| 0.0504          | 0.0507          | 0.0994          | 0.0993          |
| .0504           | .0508           | .0994           | .0993           |
| .0252           | .0253           | .0994           | .0996           |
| .0126           | .0124           | .0994           | .0994           |
| .0126           | .0126           | .0994           | .0997           |

The antimony was determined by titration with potassium bromate. Since dilute solutions of ammonium fluoride made slightly alkaline seem to have but slight action on Pyrex glass a number of separations were made in Pyrex beakers. The filtrates from the silver arsenate after removing the silver were evaporated in the large quartz dish. Although this dish has been used in a large number of determinations the inner surface still retains its highly pearly luster.

TABLE III  
SEPARATION OF ARSENIC AND ANTIMONY IN PYREX GLASS

| As taken,<br>g. | As found,<br>g. | Sb taken,<br>g. | Sb found,<br>g. |
|-----------------|-----------------|-----------------|-----------------|
| 0.0630          | 0.0635          | 0.0994          | 0.0997          |
| .0504           | .0503           | .0994           | .0997           |
| .0252           | .0254           | .0994           | .0998           |

A mixture of 0.1026 g. of arsenious oxide and 0.1203 g. of potassium acid pyroantimonate tetrahydrate was dissolved and the arsenic and antimony were precipitated with hydrogen sulfide. The sulfides were treated in a platinum dish with fuming nitric acid, most of the acid was evaporated off, 2 cc. of hydrofluoric acid and a little water were added, the solution was warmed until clear and diluted to 100 cc. After oxidizing the antimony completely to the quinquivalent state with potassium persulfate, the separation of the two elements was made as directed: As taken (as  $\text{As}_2\text{O}_3$ ) 0.0777 g.; As found, 0.0780 g.; Sb taken (as  $\text{H}_2\text{K}_2\text{Sb}_2\text{O}_7 + 4\text{H}_2\text{O}$ ), 0.0577 g.; Sb found, 0.0579 g.

<sup>15</sup> Fresenius, "Qualitative Chemical Analysis," John Wiley and Sons, Inc., New York, 1921.

<sup>16</sup> It was kept in a Pyrex flask. At the end of a month the liquid left was perfectly clear and the antimony concentration had not changed. A small, transparent, gelatinous deposit proved to be potassium silicofluoride.

If a mixture of the sulfides of arsenic, antimony and tin is to be examined, it is best dissolved in a small platinum or quartz dish in boiling concd. sulfuric acid, a piece of pure sulfur being dropped into the dish to yield sulfur dioxide which reduces the arsenic and antimony to the trivalent condition. After diluting the solution, adding hydrofluoric acid and filtering into a large platinum dish, the arsenic and antimony are reprecipitated with hydrogen sulfide and separated as above directed. The tin remains in solution and may be determined by any one of the methods proposed by McCay<sup>17</sup> and by Furman.<sup>18</sup> A mixture of the sulfides of arsenic, antimony and tin of known composition was analyzed: As taken, 0.0768 g.; As found, 0.0771 g.; Sb taken, 0.1208 g.; Sb found, 0.1215 g.; Sn taken, 0.2014 g.; Sn found, 0.2013 g.

### Summary

1. From a hydrofluoric acid solution of arsenic and antimonous acids, made weakly but distinctly alkaline with ammonia, silver nitrate in excess precipitates completely the arsenic as silver arsenate, quite free from antimony.

2. The amount of arsenic is found by dissolving the precipitate in nitric acid and determining the silver in it by the method of Volhard.

3. The filtrate from the silver arsenate, after removing the silver with a minimum amount of hydrochloric acid, is mixed with concentrated sulfuric acid and evaporated, the acid heated to strong fuming, boiled gently in the presence of a piece of sulfur and the antimonous acid titrated with potassium permanganate or potassium bromate according to the details given.

PRINCETON, NEW JERSEY

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<sup>17</sup> McCay, *THIS JOURNAL*, **31**, 373 (1909).

<sup>18</sup> Furman, *Ind. Eng. Chem.*, **15**, 1071 (1923).