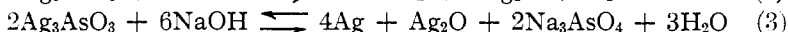
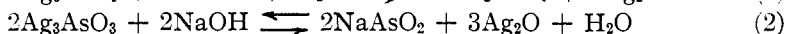
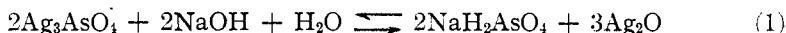


[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF NEVADA.]
THE SEPARATION AND DETECTION OF ARSENATE AND ARSENITE.

BY GEO. W. SEARS.

Received November 18, 1920.

Of the methods now available for the detection of arsenate and arsenite those based on the formation of arsine¹ and those taking advantage of the oxidizing power of arsenates² or the reducing power of arsenites³ are perhaps the most common. The limited applicability of these methods to a general separation and detection of the more common acid radicals led the author to make a study of the relative solubility of their silver salts in various concentrations of sodium hydroxide. When silver arsenite, to which potassium hydroxide has been added, is allowed to stand in the sunlight or is heated to 50° on the water-bath the arsenic slowly dissolves with the formation of potassium arsenate.⁴ No information, however, was available regarding the effect of alkaline solutions, other than ammonium hydroxide, on silver arsenate. Both salts are readily soluble in ammonium hydroxide.⁵ An examination of the 2 salts with respect to their relative solubility in excess of sodium hydroxide leads to a study of the following equilibria.



Experimental.

Preparation of Silver Arsenate and Silver Arsenite.—Weighed amounts of the C. P. sodium salts were dissolved in enough water to make a concentration of 10 mg. of the acid radical per cc. of solution. Definite volumes of these solutions were diluted, acidified with nitric acid and an excess of silver nitrate was added. To the resulting mixture sodium hydroxide was added drop by drop with constant stirring until the black precipitate of silver oxide just failed to redissolve. The appearance of the black silver oxide is very definite and easy to detect, and hence makes a very satisfactory indicator. Under these conditions the solution has an acidity of about 10^{-6} to 10^{-7} . It reacts acid toward phenolphthalein and basic toward methyl orange. With congo red an orange to violet color is obtained. Both silver arsenate and silver arsenite are completely precipitated⁶ and can be filtered with ease. The salts obtained in this way and containing a definite weight of the acid radical were removed from the filter by means of a fine stream of water. This resulted in a rather finely divided suspension to which the solvent was added.

Solubility of Silver Arsenite.—Approximately 6 N sodium hydroxide

¹ *Chem. Ztg.*, **33**, 1209; *Z. anal. Chem.*, **41**, 362 (1902).

² *Am. J. Sci.*, [3] **48**, 216 (1894).

³ *Ibid.*, [4] **1**, 35 (1896).

⁴ *Ber.*, **27**, 1019 (1894).

⁵ "Dictionary of Chemical Solubilities," Comey, pp. 37-42.

⁶ The filtrate does not give a precipitate with H₂S.

solution was added to the precipitate of silver arsenite suspended in 10 to 20 cc. of water as indicated above, and after a thorough mixing, the mixture was filtered and both precipitate and filtrate tested for arsenic as follows. The precipitate was leached with 6 *N* hydrochloric acid to dissolve the arsenic and remove the silver. The clear solution was then saturated cold with hydrogen sulfide. The filtrate was strongly acidified with hydrochloric acid and saturated with hydrogen sulfide. Table I shows the behavior of silver arsenite toward various concentrations of sodium hydroxide. The residue invariably gave a positive test and the filtrate a negative test, except in the last experiment, when the filtrate gave a positive test.

TABLE I.

Mg. AsO ₃ %	Cc. of approx. 6 <i>N</i> NaOH.	Total volume. Cc.	Approx. normal strength.
0.5	0.2	10	0.12
1	0.2	10	0.12
10	0.2	10	0.12
100	0.2	10	0.12
0.5	0.5	10	0.3
10	0.5	10	0.3
100	0.5	10	0.3
0.5	1	25	0.24
100	1	25	0.24
1	2	25	0.48
1	5	25	1.2
50	5	20	1.5
50	5	15	2

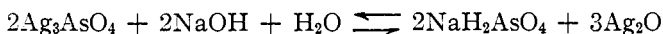
The results obtained show that cold sodium hydroxide up to about 1.5 *N* has no solution effect on silver arsenite, though higher concentrations seem to have a slight solvent action. In Reichard's work¹ on the action of potassium hydroxide on silver arsenite no statement is made regarding the concentration of potassium hydroxide solution used, hence it seemed advisable to repeat a part of his work, using small concentrations of sodium hydroxide solution. The results obtained from a number of experiments showed that at the temperature of the water-bath silver arsenite is slowly dissolved in 0.5 *N* sodium hydroxide solution. The reaction proceeds almost entirely according to Equation 3 above, as shown by the fact that only a trace of arsenic could be detected by precipitation with hydrogen sulfide from a cold hydrochloric acid solution while a considerable amount of metallic silver was left in the residue. On the other hand, when the mixture was kept cold no reaction was detected in concentrations of sodium hydroxide below 1.5 *N* and in higher concentrations (4–6 *N*) reaction according to Equation 2, seemed to predominate, although the presence of small amounts of metallic silver in the residue showed that some arsenic was dissolved according to Equation 3. Even

¹ Reichard, *Ber.*, 27, 1019 (1894).

in 6 *N* sodium hydroxide solution only a small fraction of the silver arsenite present was dissolved.

Solubility of Silver Arsenate.—In the investigation of the solubility of silver arsenate experiments were carried out in the same manner as those with silver arsenite except that the residue after leaching with hydrochloric acid was heated to boiling before saturating with hydrogen sulfide. The filtrate was acidified with acetic acid and the arsenate precipitated with uranyl acetate. The resulting uranyl arsenate was then dissolved in hydrochloric acid and arsenic precipitated with hydrogen sulfide as before. Preliminary experiments showed that some silver arsenate dissolved even in very small concentrations (0.05 to 0.1 *N*) of sodium hydroxide but seemed to indicate incomplete solution when as much as 5 mg. of the arsenate radical was present. With 0.5 to 1 mg. of arsenate, solution was complete as shown by a negative test on the residue and a positive test in the filtrate. When 50 to 100 mg. was used a considerable proportion seemed to dissolve, but in all cases the residue gave a positive test. Increasing the concentration of the sodium hydroxide made very little change in these results, while increased dilution of the arsenate seemed to give a greater solution effect.¹

The result of preliminary experiments indicated that an equilibrium was established in which perhaps 75 to 80% of the arsenate was dissolved. It seemed worth while, therefore, to make a more careful study of the equilibrium



in order to find out if possible the conditions under which it might be shifted to the right and complete solution of the arsenate be obtained. To this end several experiments were carried out as described above.

TABLE II.

AsO ₄ '' Mg.	Cc. of approx. 6 <i>N</i> NaOH.	Total volume. Cc.	Approx. normal strength.	Residue.
0.5	0.3	10	0.18	Neg.
1	0.3	10	0.18	Neg.
1	0.25	25	0.06	Neg.
10	0.5	25	0.12	Neg.
25	0.5	25	0.12	Pos.
50	1	25	0.24	Neg.
100	1	25	0.24	Neg.
150	1	25	0.24	Pos.
150	2	25	0.48	Neg.
200	2	25	0.48	Neg.
250	2	25	0.48	Pos.
400	3	25	0.72	Neg.
450	3	25	0.72	Neg.
1	0.13	25	0.03	Pos.

¹ Later work showed that these results were due in large measure at least to insufficient washing of the silver oxide residue.

Various concentrations of sodium hydroxide were added to the precipitate of silver arsenate, suspended in water, and the mixture was well stirred before filtering. The silver oxide residue was then washed till the wash water gave no further test for alkali with litmus paper.

Table II shows the behavior of silver arsenate toward various concentrations of sodium hydroxide. The filtrate gave a positive test in every experiment except the last, which was negative.

It may be seen from the above results that the solvent action of sodium hydroxide on silver arsenate increases very rapidly with increasing concentration and is appreciable at concentrations as low as 0.06 *N*. No action is apparent, however, in 0.03 *N* sodium hydroxide solution.

Discussion.

From the foregoing results it is evident that a quantitative separation of arsenate and arsenite may be obtained by the action of sodium hydroxide solution (0.5–1.5 *N*) on their silver salts, the arsenate passing into solution. Higher concentrations of sodium hydroxide react slowly with silver arsenite with the formation of a mixture of soluble trivalent and pentavalent arsenic, probably according to Equations 2 and 3 above. Even very high concentrations, however, seem to have but slight solvent action in the cold.

It would seem, therefore, that some influence other than is apparent in the equilibrium represented by Equation 1 must come into action to affect the solution of silver arsenate since similar forces seem to act in the opposite direction in Equation 2. A compound of the formula $(As_2O_5)_2 \cdot 3NaOH$ has been described by Filhol and Senderens¹ as being formed by the action of excess sodium hydroxide on arsenic acid. They obtained it in crystalline form only after evaporation to a sirupy consistency. No evidence of a similar action with arsenious acid was found. This difference in tendency toward complex formation with sodium hydroxide may, therefore, account for the difference in solubility of the silver salts. Without the formation of a complex ion the equilibrium represented in Equation 1 should shift toward the less soluble silver salt as is apparently the case in Equation 2.

Procedure.

(1) **Precipitation.**—To a nitric acid solution of the acids containing an excess of silver nitrate add sodium hydroxide drop by drop from a pipet until on shaking the dark silver oxide precipitate just fails to redissolve. Filter, wash the precipitate and transfer it to a graduate cylinder by means of 15 to 20 cc. of water from a wash bottle. Add 2 to 3 cc. of approximately 6 *N* sodium hydroxide solution and fill up to the 25 cc. mark with water. The amount of sodium hydroxide that should be added depends on the quantity of arsenate present. More than 450 mg. of arsenate is completely dissolved in 25 cc. of solution containing 3 cc. of 6 *N* sodium hydroxide solution while as much as 5 cc. of the alkali in 25 cc. of solution produces no solvent action on the

¹ Filhol and Senderens, *Compt. rend.*, 93, 388 (1881).

arsenite. Transfer the contents of the cylinder to a beaker and mix thoroughly. Filter, and wash the residue free from alkali. Test the residue for arsenite and the filtrate for arsenate.

(2) **Detection of Arsenite.**—Dissolve the residue of silver arsenite (1) by pouring a 5-cc. portion of 6 *N* hydrochloric acid repeatedly through the filter and add hydrogen sulfide to the clear solution obtained. If a dark precipitate is obtained showing the presence of heavy metal sulfides insoluble in hydrochloric acid, it may be tested for arsenic according to the usual methods.

(3) **Detection of Arsenate.**—The filtrate from (1) contains the arsenate which may be separated by acidifying with acetic acid and adding uranyl acetate in slight excess. The arsenate is precipitated as uranyl hydrogen arsenate, UO_2HAsO_4 . If the precipitate should be colloidal or finely divided it may be collected and readily filtered by shaking with a pinch of asbestos fiber. The uranyl arsenate is readily soluble in hydrochloric acid from which it may be precipitated as sulfide by means of hydrogen sulfide.

The method has been successfully used by the author's classes in qualitative analysis as a means of detecting arsenate and arsenite either alone or in the presence of each other.

Summary.

A procedure is described for the separation and detection of arsenate and arsenite.

The separation is based on the relative solubility of their silver salts in sodium hydroxide.

Data in support of the procedure are furnished. The method is capable of detecting 1 mg. of either ion in the presence of 450 mg. of the other.

RENO, NEVADA.

NOTES REGARDING THE CONSTRUCTION OF PLATINUM RESISTANCE THERMOMETERS AND IMMERSION HEATING COILS OF LOW LAG.¹

By T. S. SLIGH, JR.

Received November 23, 1920.

This paper describes briefly some recent modifications in the construction of platinum resistance thermometers which have been found desirable on account of a gain in accuracy, simplification of construction, or of greater mechanical strength.²

Strain-free Thermometers.

All thermometers are of the potential terminal type as the use of this type with a potentiometer or a wheatstone bridge with reversing commutator offers complete elimination of the effects of lead resistance.

Changes in the construction of the strain-free type of thermometer from that described in Bureau of Standards *Bulletin* 6, p. 150 (1909),

¹ Published by permission of the Director, Bureau of Standards.

² See *Scientific Paper* No. S-407 of the Bureau of Standards for a more detailed treatment of this subject.