that the ions are much more complex than would be expected from the oxonium theory.

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THE DECOMPOSITION OF TETRATHIONATES IN ALKALINE SOLUTION AS A SOURCE OF ERROR IN CERTAIN IODINE TITRATIONS.[1]

By Robert M. Chapin.

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It has long been known that tetrathionates are not stable. Particularly has Gutmann[2] shown that sodium tetrathionate rapidly reacts with moderately concentrated hot caustic soda to form sodium thiosulfate and sodium sulfite. But that the reaction might progress with significant rapidity in cold and dilute solutions seems to have remained unsuspected; at any rate, no allowance is made for such a possibility in certain methods of quantitative analysis. For example, it is a very common procedure to determine arsenic in a variety of materials by some modification of the process described by Williamson.[3] Iodine resulting from the use of hydriodic acid as a reducing agent is removed by sodium thiosulfate, following which the solution is in practice frequently rendered decidedly alkaline before being brought to the proper condition for titration.

Some time ago, following the official directions of the Assoc. Offic. Agr. Chemists[4] for the estimation of "total arsenious oxide" in insecticides and fungicides, the writer became impressed with the fact that the method, as laid down, did not afford the uniformly accurate results promised by the theory of the process. He found that substitution of sodium sulfite for thiosulfate as a discharging agent for iodine produced a distinct improvement in results and acted accordingly in work[5] in which accuracy was particularly necessary. Later, incidental to other work,[6] he showed that tetrathionates are in fact rather rapidly affected by exposure at room temperature to comparatively low concentrations of hydroxyl ions. The purpose of the present paper is to extend these observations sufficiently to form a guide to correct procedure in iodometric methods, etc., involving the conditions outlined.

Tetrathionate solution (0.0519 *N*) was prepared by titrating iodine

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[1] Published by permission of the Secretary of Agriculture.

[2] *Ber.*, 40, 3614 (1907).

[3] Sutton, "Volumetric Analysis," 10th Edition, p. 156.

[4] Bur. of Chemistry, *Bull.* 107 (Revised), Reprint January 18, 1912, p. 25.

[5] *J. Ind. Eng. Chem.*, 6, 1002 (1914).

[6] *Ibid.*, 8, 151 (1916).

solution (0.1022 *N*) with sodium thiosulfate solution (0.1054 *N*), without starch. Portions of 20 cc. of tetrathionate solution were measured into flasks, diluted, and mixed with measured amounts of solutions of alkalies or alkaline salts, the final volume in each case being 100 cc. The temperature of the laboratory and solutions was somewhat over 30°. The mixture in each flask was left standing 15 minutes, after which it was acidified with dilute hydrochloric acid and methyl orange, then titrated with standard iodine and starch.

Character of medium.	Cc. 0.1022 *N* iodine.	Character of medium.	Cc 0.1022 *N* iodine.
Blank	1 drop	NH_4OH, 0.1 *N*	0.95
NaOH, 0.1 *N*	9.21	$NaHCO_3$, 0.5 *N*	2 drops
NaOH, 0.01 *N*	3.98	$NaHCO_3$, 0.1 *N*	1 drop
Na_2CO_3, 0.1 *N*	5.20	$NaHCO_3$, 0.5 *N*, plus[1] CO_2	1 drop
Na_2CO_3, 0.01 *N*	0.50		

It is clear that tetrathionates are notably sensitive to even low concentrations of hydroxyl ions, though only slightly affected by sodium bicarbonate, and still less by sodium bicarbonate in presence of carbonic acid. It therefore follows that acid solutions containing tetrathionates, if to be later titrated with iodine, or subjected to any treatment involving assumption that the tetrathionate present has remained unaffected, should never be neutralized by any substance of distinctly alkaline properties. Significant errors may not necessarily result, but a source exists which can produce grave errors through incautious manipulation. Sodium bicarbonate within reasonable limits of excess is appropriate, provided the solution be not left at an elevated temperature a considerable length of time. As a discharging agent for iodine, under such conditions as prevail in the determination of arsenic, it seems safer to abandon the use of thiosulfate altogether, and to substitute therefor a dilute solution of sodium sulfite—about 0.5% of the anhydrous salt.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF MINNESOTA.]

NONIDEAL SOLUTIONS. THE ACTIVITY OF A DIFFICULTLY SOLUBLE COMPONENT.

BY E. K. STRACHAN.

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I. Introduction.

The study of the colligative properties of solutions has been greatly facilitated by use of the concept of the ideal solution.[2] This concept

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[1] (50 cc. *N* $NaHCO_3$ saturated with CO_2 before added to diluted tetrathionate.)

[2] E. W. Washburn, THIS JOURNAL, 32, 660 (1910); G. N. Lewis, *Z. physik. Chem.*, 61, 129 (1907).