III, where they are compared with the corresponding distances in potassium fluoride.[8]

TABLE III

THE DISTANCES BETWEEN THE ATOMS

	K and F	K and K	F and F
In KHF_2	2.77	3.41 4.01	2.25
In KF	2.68	3.79	...

Summary

The positions of the potassium and fluorine atoms in tetragonal potassium hydrogen fluoride, KHF_2, have been determined by means of X-rays. The dimensions of the unit are 5.67 × 5.67 × 6.81 Å. The structure may be described as an ammonium chloride arrangement of potassium atoms and fluorine dumb-bells, the two atoms of each dumb-bell lying in a plane perpendicular to the tetragonal axis. For the hydrogen atoms there are two possible positions, one of which is in the middle of the dumb-bell, forming an HF_2^- ion. The distances in Ångstrom units between the atoms are summarized in Table III.

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[CONTRIBUTION FROM SANDERS CHEMICAL LABORATORY, VASSAR COLLEGE]

THE STABILITY OF SODIUM THIOSULFATE SOLUTIONS

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The present investigation was undertaken as a critical study of the stability of 0.01 *N* sodium thiosulfate under the conditions of its use as a standard solution in an analytical laboratory. It was also hoped that the investigation might throw some light on the mechanism of the decomposition.

Topf[1] in 1887 proved that the carbon dioxide of the air could not account for the deterioration, and concluded that it was to be attributed to direct oxidation: $Na_2S_2O_3 + O \longrightarrow Na_2SO_4 + S$. He also noticed that the fall in normality was greater in summer than in winter. Kolthoff[2] made an extensive study of the behavior of 0.1 *N* and 0.01 *N* sodium thiosulfate solutions under various conditions and in the presence of a great number of substances. He found that sunlight hastened the decomposition; that 0.01 *N* solutions decomposed much more rapidly than 0.1 *N*; that small amounts of mercuric iodide greatly retarded the decomposition, as did small amounts of alkaline substances; that salts of the heavy metals

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[8] Wyckoff, *J. Washington Acad. Sci.*, **12**, 251 (1922).

[1] Topf, *Z. anal. Chem.*, **26**, 137 (1887).

[2] Kolthoff, *Pharm. Weekblad*, **56**, 878 (1919); *Z. anal. Chem.*, **60**, 344 (1921).

had various effects; that the sulfur deposit from decomposed thiosulfate solutions accelerated the decomposition, and that carbon dioxide had little influence. He suggested that the decomposition might be due to certain sulfur-consuming microörganisms. He recommended that in preparing the solution 10 mg. of mercuric iodide or 200 mg. of sodium carbonate be added per liter, and that the flasks be sealed and kept in the dark.

Rice, Kilpatrick and Lemkin[3] studied the behavior over a period of 52 days of 0.01 *N* solutions of sodium thiosulfate made up with different grades of distilled water. Using the same method of analysis, the authors have continued this study for some 200 days. The results,[4] which in general are similar to those already given, are summarized in the following table.

TABLE I

EFFECT OF DIFFERENT GRADES OF DISTILLED WATER

	Distilled water	Initial titer, Oct. 3, 1922 *N*	Final titer, May 31, 1923 *N*	Fall %
1	Laboratory	0.012401	0.009848	20.6
2	Redistilled	.013248	.011810	10.9
3	Redistilled, freshly boiled	.014085	.014016	0.5
4	Redistilled, through which CO_2-free air had been bubbled	.013111	.012866	1.9

At the same time a fifth bottle was prepared in the same way as in Expt. 1, was sealed, and set aside. Six months later it was opened, fitted with a soda-lime tube and siphon, and a portion was analyzed in the usual way. The normality was found to be 0.012688. In 40 days the normality dropped to 0.012512, a decrease of 1.4%. This is distinctly at variance with the result reported by Treadwell[4] for a 0.1 *N* solution.

During the period of investigation, portions were drawn off from the bottles for other experiments. At the end of the work the air spaces above the solutions varied from 4 to 10 liters. (We mention this because it would be the usual case in the laboratory.) Considerable deposits of sulfur formed in Bottles 1, 2 and 5, while no deposit was apparent in 3 or 4. The hydrogen-ion concentration of the solutions, determined colorimetrically from time to time, showed no appreciable change.

The most stable of the solutions, 3, was selected for the purpose of testing the effects of carbon dioxide, of oxygen, and of small quantities of alkali on the titer of 0.01 *N* sodium thiosulfate solution. Portions of the solution through which carbon dioxide and oxygen, respectively, had been bubbled for several hours were siphoned into glass-stoppered tubes. At intervals a tube was opened and its contents analyzed. In the case of the alkali, a weighed amount of standard sodium hydroxide solution was added to

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[3] Rice, Kilpatrick and Lemkin, THIS JOURNAL, **45**, 1361 (1923).

[4] Treadwell-Hall, "Analytical Chemistry," Wiley and Sons Co., fifth ed., **1919**, vol. 2, p. 645.

a weighed amount of thiosulfate, and the resulting solution, 0.001 *N* in sodium hydroxide, was siphoned into tubes, as before. The analysis of the alkaline solution was carried out in a slightly different manner. As Kolthoff[5] has pointed out, in 0.01 *N* solution the minimum hydrogen-ion concentration at which iodine oxidizes thiosulfate quantitatively to tetrathionate is 3.16×10^{-7}; at lower concentrations of hydrogen ion the thiosulfate is partially oxidized to sulfate. Kolthoff showed that the error is much less when the thiosulfate is titrated with iodine than in the reverse procedure. In his work with slightly alkaline thiosulfate, Kolthoff ran the thiosulfate into an excess of acidified iodine and titrated back with thiosulfate. In the present investigation the thiosulfate was run into a suitable buffer and was titrated directly with iodine. The results of the experiments are given in Table III. For purposes of comparison, data for the original solution over the same period are included.

TABLE II

EFFECTS OF CARBON DIOXIDE, OF OXYGEN AND OF SODIUM HYDROXIDE

Date	Original solution No. 3 *N*	Solution treated with CO_2 on Mar. 3 *N*	Solution treated with O_2 on Feb. 27 *N*	Solution 0.001 *N* in NaOH; prepared Feb. 28 *N*
Mar. 3	0.014005	0.014020	0.013998	(0.013938, calc.)
10	.....	.014035	.013987	.....
17	.014014	.....	.....	.013944
28	.014005	.014035	.013995	.013931
Apr. 28	.014013	.014028	.013955	.013910

It is evident that carbon dioxide, oxygen and sodium hydroxide have very little effect on a stable solution of sodium thiosulfate. The slight effect observed in the case of carbon dioxide is in agreement with the results of Topf and of Kolthoff. It is, however, contrary to the results of Hahn and Windisch,[6] who report an increase of 10% over a period of 51 days in the normality of a 0.02 *N* solution of sodium thiosulfate, half saturated with carbon dioxide. The same authors, however, report a gain of approximately 9% for a 0.02 *N* solution of sodium thiosulfate in distilled water. As far as we know, only one other such case appears in the literature, that of Waterman.[7]

During the course of these experiments, a bacteriological examination revealed the fact that the bacterial count of all the solutions was high, and that the solution which was decomposing most rapidly, No. 1, contained by far the greatest number of organisms. In addition, it appeared to give a pure culture. The organism was isolated, as was another organism from Solution 2. Two sterilized portions of Solution 4 were inoculated with these organisms and were kept at 21° for 24 hours. One-cc.

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[5] Kolthoff, *Pharm. Weekblad,* **56,** 572 (1919).

[6] Hahn and Windisch, *Ber.,* **55,** 3163 (1922).

[7] Waterman, *Chem. Weekblad,* **15,** 1098 (1918).

portions of the inoculated solutions were added to 500–600 cc. of Solution 4 in 2 glass-stoppered liter bottles. The following table shows the changes in normality observed in a month's time.

Table III

Changes in Normality in One Month's Time

Date	600 cc. of Soln. 4 + 1 cc. inoculated with bacteria from Soln. 1 *N*	600 cc. of soln. 4 + 1 cc. inoculated with bacteria from Soln. 2 *N*
Apr. 11	0.012934	0.012934
18	.012921	.012931
May 2	.012284	.012872
12	.011848	.012716
	Fall, 8.3%	Fall, 1.6%

During the same period the normality of the original solution, 4, decreased by 0.3%. It is evident that the decomposition is due to the action of bacteria.[8]

The authors wish to thank Dr. E. M. Twiss of Vassar College for her help with the bacteriological work.

Summary

The stability of several 0.01 *N* solutions of sodium thiosulfate has been studied over a period of 8 months.

Freshly boiled redistilled water gave a solution that was more permanent than that obtained with laboratory distilled water, ordinary redistilled water or redistilled water through which carbon dioxide-free air had been bubbled.

Carbon dioxide, oxygen or dilute sodium hydroxide had very little effect on the stability of the solution.

Decomposition is caused by the action of bacteria.

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NOTE

A Glass-to-Metal Joint.—In a recent note by Merle L. Dundon[1] on a glass-to-metal joint it was claimed that the method of McKelvy and Taylor[2] of platinizing, copper plating and soldering was tried without success. The failure of the joints by cracking of the glass upon cooling was ascribed to heat strains introduced by the soldering process. Heat strains may be introduced during the platinizing process, if the glass is not cooled carefully, but the temperature of melted tin is not sufficiently

[8] The organism isolated from Solution I has been identified by Selman A. Waksman, at the New Jersey Agricultural Experiment Station, as *Thiobacillus thioparus*. Its characteristic reaction is the transformation of thiosulfate into sulfate and elementary sulfur.

[1] Dundon, This Journal, **45**, 716 (1923).

[2] McKelvy and Taylor, *ibid.*, **42**, 1364 (1920).