[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY]

THE ESTIMATION OF IODINE BY SODIUM THIOSULFATE

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In the course of a study of reaction velocities we found it necessary to make a large number of titrations of iodine solutions against sodium thiosulfate. Owing to the troublesome volatility of the iodine we made a preliminary investigation of methods of handling and estimating iodine solutions. We also investigated the stability of sodium thiosulfate solutions, since a survey of recent literature shows a lack of agreement on these points.

Washburn[1] finds that an iodine solution containing 2% of potassium iodide, properly used, is one of the most stable of standard solutions. Chapin[2] discusses the precautions necessary in the preparation and use of standard iodine solutions. He points out that the amount of potassium iodide added is important, since its action is not only to dissolve the iodine but also to lower its vapor pressure and prevent ready volatilization of the iodine. He shows that the proportion of double the weight of iodine in 0.1 and 0.05 N solutions which was authoritatively recommended was too low and suggests 4% of potassium iodide for solutions in which a high degree of permanence is desired.

Regarding the stability of sodium thiosulfate, Treadwell[3] recommends that a freshly prepared solution be allowed to stand for 8–14 days before standardization and gives equations purporting to show that the carbon dioxide present in the water is "used up" during this period, and thereafter the solution is stable. If these equations are written ionically it will be readily seen that the carbon dioxide is not used up and consequently the solution should continue to decompose indefinitely.

Foulk and Morris[4] found that their thiosulfate which was 2 years old decomposed at a rate corresponding to a fall of over 0.6% over a period of 8 months. Kolthoff[5] studied the effect of the addition of many substances on the stability of sodium thiosulfate. He claims that the presence of 0.01 N sodium hydroxide, or 0.005 N sodium carbonate prevents any decomposition of the solution over a period of 4 months. Treadwell[3] states, "Frequently the addition of ammonium carbonate is recommended in order to obtain a more permanent solution; it has the opposite effect." Hahn and Windisch[6] studied the effect of adding carbon dioxide, and also alkalies, to standard thiosulfate solution. They found that carbon dioxide, 0.01 N sodium bicarbonate, 0.01 N sodium hydroxide and 0.01 N sodium carbonate all caused gradual decomposition of the thiosulfate, but that very small quantities of sodium carbonate (0.00002) stabilized the solution. This indicates that in neutral solution sodium thiosulfate is stable. They also claim that in all the cases investigated the thiosulfate solutions attained a constant titer after standing for about 1 month, but our results do not support this claim.

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[1] Washburn, THIS JOURNAL, **30**, 40 (1908).

[2] Chapin, *ibid.*, **41**, 357 (1919).

[3] Treadwell, "Analytical Chemistry," J. Wiley and Sons Co., fifth edition, vol. 2, p. 645.

[4] Foulk and Morris, *ibid.*, **44**, 221 (1922).

[5] Kolthoff, *Z. anal. Chem.*, **60**, 344 (1921).

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

Analytical Procedure.—In these titrations the loss of iodine was remedied by delivering the iodine solution, without exposure to the air, directly into the sodium thiosulfate solution. The procedure was as follows. Each of the bottles containing the iodine and thiosulfate solutions was fitted with a siphon terminating in a stopcock, the tip of which was drawn out to be 15 cm. long, with internal and external diameters of 0.5 and 1.5 mm., respectively. Portions of thiosulfate solution, 10–30 g., were weighed to 0.005 g. in a stoppered conical flask of 250cc. capacity containing 2 cc. of starch solution made according to the method of Chapin.[2] Before adding the iodine to the thiosulfate we first filled the tip of the siphon from the iodine bottle, by adding a little of the iodine to a beaker of water, keeping the glass tip about 1 cm. beneath the surface of the water. When removing the beaker we touched the end of the tip with the edge of the beaker to detach any adhering liquid. Immediately we ran the iodine from the stock bottle into the weighed thiosulfate solution keeping the tip about 1 cm. under the liquid until a faint blue color appeared. When removing the flask we again touched the tip against the side to remove adhering liquid. By weighing the flask again we obtained the weight of iodine added, and from blank experiments determined the small correction for the excess of iodine. The advantages of this procedure are (1) a weight buret is not needed, (2) a final titration with dilute thiosulfate is unnecessary, (3) loss of iodine vapor and splashing are avoided, and (4) the iodine is not added in drops but in such small quantities that the solution can be brought to the faintest pink.

We found this procedure to be quite satisfactory and rapid. Its accuracy was demonstrated by successive titrations of a 0.1 *N* solution of iodine in a 4% solution of potassium iodide. The mean value of the normality of the iodine obtained from 8 such titrations[7] was 0.09524, with an average deviation of 0.025%.

Loss of Iodine from Solutions Containing Potassium Iodide

Using this accurate procedure, we have carried out a number of experiments to show how readily iodine is lost from solutions containing potassium iodide, if less care is exercised. In Expts. a to d, inclusive, 0.1 *N* iodine containing 4% of potassium iodide was titrated with 0.1 *N* thiosulfate solution.

(a) Thirty g. of the iodine solution was run into the 250cc. conical flask and swirled gently for 1 minute, unstoppered. The iodine was then estimated; two such titrations gave iodine, 0.09501 *N*, av. dev., 0.035%. This shows a loss of 0.22%. Two more experiments were performed similarly except that the flask was kept stoppered while the iodine solution was swirled. They gave the same result.

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[7] All titrations in this paper are expressed in terms of weight normality.

(b) Two experiments were performed in which the iodine solution was dropped into the thiosulfate from a height of a few centimeters. Two titrations gave the iodine 0.09528 *N*, av. dev., 0.031%. These showed no loss.

(c) About 50 cc. of the iodine solution was placed in a clean, dry 100cc. beaker and left for 15 minutes in a room free from drafts. A glass plate fixed a few centimeters above the beaker prevented particles of dust from falling into the solution. On titration, the iodine was found to be 0.09438 *N*, showing a loss of 0.91%.

(d) We then performed a similar experiment but allowed the iodine solution to stand for 2 hours. The iodine was found to be 0.09123 *N*, showing a loss of 4.2%. It is evident from these results that even when 0.1 *N* iodine contains 4% of potassium iodide, great care is necessary in handling it if loss of iodine is to be prevented. We found that the iodine in the stock bottle maintained its strength until the bottle was $^1/_3$ full, when the strength fell gradually as the bottle was further emptied.

(e) We repeated the foregoing experiments using 0.1 *N* iodine containing 2% of potassium iodide. We found that this concentration is almost as effective as 4% in diminishing the volatility of the iodine.

(f) The experiments were repeated, except that 0.01 *N* iodine containing 0.025 *M* potassium iodide was titrated with 0.01 *N* thiosulfate solution. Iodine vapor is clearly visible above such a solution. The ease with which iodine is lost is shown by the change in the normality of thiosulfate solution found when the iodine solution was dropped at various rates into the thiosulfate from a height of a few centimeters: very quickly, 0.010548; quickly, 0.010527; slowly, 0.010500; drop by drop, 0.01049.

By simply falling through a few centimeters of air these solutions may lose up to 0.5% of their iodine. They cannot be kept in a partly filled bottle or exposed to the air without rapid loss of iodine.

(g) We made up solutions of iodine containing low concentrations of hydrochloric acid (0.01–0.04 *N*) and titrated them in the usual way. We found that in the presence of the acid more thiosulfate was required for a given quantity of iodine solution, the increase depending on the amount of acid present. In order to overcome this difficulty we devised the following procedure.

A stoppered conical flask containing 2 cc. of starch solution and 50 cc. of a neutral buffer solution was weighed. About 20 cc. of thiosulfate was added and the flask weighed again. The acid iodine solution was then run in through a titrating siphon until the solution was faintly blue. A final weighing and blank correction were then made. Using this method we showed that it was immaterial whether the iodine was acid or not. Other experiments, in which the buffer solution was mixed with thiosulfate solution for several days before titration, showed that there was no decomposition of the thiosulfate. Six titrations of neutral iodine with thiosulfate gave the normality of the iodine as 0.10229. Five more titrations were made in which various quantities of buffer solution were added to the thiosulfate. The mean value for the iodine was 0.10225 *N*. The buffer solutions used were the phosphate buffer and boric acid buffer described by Washburn.[1] With these buffer solutions mixed with the thiosulfate, it is possible to titrate iodine quantitatively in neutral solution or in solutions of various degrees of acidity.

Stability of Thiosulfate Solutions

In order to test the effect of carbon dioxide we passed the gas through standard thiosulfate solutions for various periods (1 minute to 4 hours) but found no alteration in strength. In one case we passed carbon dioxide through a thiosulfate solution for 4.5 hours and allowed the solution to stand for 17 hours more before titration. It lost only 0.2% in this period.

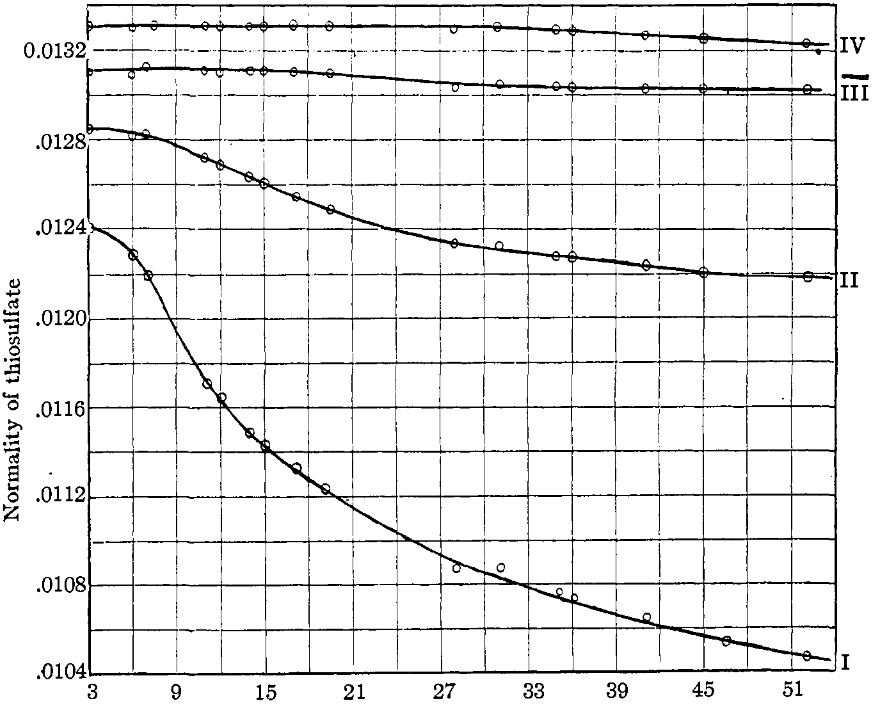

Fig. 1.—The normality of points on Curve I is given directly from the ordinate. The correction for points on Curve II is +0.0004, Curve III +0.001, Curve IV —0.0002.

We then assumed that the decomposition of thiosulfate was due to hydrogen ion as represented by the following equation: $S_2O_3^{--} + H^+ =$

$SO_3^{--} + S + H^+$. If this equation represents the action, we should expect the addition of acid to cause the solution to become stronger, and finally reach a strength twice that of the original, assuming of course that no simultaneous reactions occurred. The reaction would apparently be monomolecular, since the concentration of hydrogen ion is constant and the velocity would be proportional to the concentration of the thiosulfate ion.

In a preliminary experiment we allowed 0.1 *N* thiosulfate solution to stand in contact with 0.01 *N* hydrochloric acid for about 5 minutes. We then neutralized with buffer solution and titrated with iodine. The strength of the thiosulfate solution had increased about 8%. We filled a number of small stoppered tubes with a 0.01 *N* thiosulfate solution in air-free water containing 0.01 *N* hydrochloric acid, and made titrations at definite time intervals. The titer of the thiosulfate increased to a maximum (about 16% increase) at the end of about 4 hours and then slowly diminished. The action is not, therefore, the simple one suggested but is complicated by simultaneous reactions. This is being studied by one of us (M. K.) in a separate investigation.

We have compared the stability of thiosulfate solutions prepared in different ways, by making titrations according to our improved technique as outlined above, over an interval of 50 days after the preparation of the solutions. Our results are shown in Fig. 1, where the observed normalities of the thiosulfate solutions are plotted against their age. Curve I represents a solution prepared from ordinary laboratory distilled water, Curve II from redistilled water, Curve III from redistilled water boiled free from dissolved gases, and Curve IV from redistilled water through which air free from carbon dioxide had been drawn for several hours.

Summary

1. We have shown that iodine solutions have an appreciable vapor pressure of iodine, and have developed a method of handling and estimating these solutions.

2. For 0.1 *N* iodine solutions, 2% potassium iodide is almost as effective as 4% potassium iodide for diminishing the vapor pressure of iodine.

3. Iodine may be estimated in acid solution if it is added to a standard thiosulfate solution in presence of a buffer solution.

4. Standard thiosulfate should be made up with the purest water obtainable. It may then be standardized and used at once.

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