tions of the theory of solutions, and to be satisfied for the present with the purely qualitative statement that the solubility product shows a diminishing value with increased concentration of other electrolytes.

Conclusion.

The results of the foregoing paper may be summarized as follows:

(1) Determinations have been made of the solubility of thallous chloride in acetic acid solutions of varying concentrations, and of tetramethylammonium iodide in potassium hydroxide solutions of varying concentrations.

(2) The electrical conductivity of tetramethylammonium iodide has been measured.

(3) The solubility product has been shown to have a value which diminishes with increase in the total concentration of electrolytes present.

I am indebted to Mr. George Barmeyer and to Mr. Charles E. Roake for the solubility determinations of Tables I and II.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 54.]

A VOLUMETRIC METHOD OF DETERMINING IODIDE IN THE PRESENCE OF CHLORIDE, BROMIDE, OR FREE IODINE.

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The method here described of determining iodide depends upon its oxidation to iodine in acid solution by means of potassium permanganate, the removal of the liberated iodine from the aqueous phase by carbon tetrachloride, and the titration of this iodine with a standard sodium thiosulphate solution. When the iodide contains free iodine dissolved in it this titration gives the total iodine present in solution; the dissolved iodine is determined by direct titration of the original solution with thiosulphate, and the difference between the two results gives the iodine present as iodide.

This method was suggested and used by Sammet,[1] but he gave no specific directions and no indication of its accuracy. A similar method was developed long ago by Fresenius,[2] in which carbon disulphide took the place of carbon tetrachloride, excess of nitrous acid was used instead of an equivalent amount of permanganate, and the nitrous acid in contact with the carbon disulphide was removed by repeated decantations with water. Information with regard to the accuracy of this method appears to be lacking, but it is doubtful if it would have, even if modified, any advantages over the present method.

The possibility of determining iodide in the presence of chloride or

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[1] Sammet; *Z. physik. Chem.*, **53**, 684 (1905).

[2] Fresenius, *Quant. Anal. 4th reprint* (1900) of 6th edit. (1875), **page** 482.

bromide depends upon the extremely rapid rate, even in dilute solutions, of the reaction

$$5I^- + MnO_4^- + 8H^+ = 2\frac{1}{2}I_2 + Mn^{++} + 4H_2O,$$

and the relatively slow rates of the corresponding reactions with chloride or bromide. The reaction with chloride is so slow that there is no appreciable liberation of chlorine, even in a moderately concentrated sulphuric acid solution. In the case of bromine, however, in order to prevent the rapid liberation of bromide, it is necessary to keep the concentration of bromide and of sulphuric acid small, and to add only a slight excess of permanganate. It will be seen later that none of these precautions introduces any difficulty.

This plan of regulating the rate of reaction between halides and permanganate by means of the hydrogen ion concentration has already been used in a well-known method of detecting the halides in the presence of each other,[1] which was developed by Jannasch and Küster.[2] In this process the halogens are expelled successively from a boiling solution: iodine from a solution containing acetic acid and sodium acetate, bromine from a solution containing acetic acid and a little sulphuric acid, and chlorine from a concentrated sulphuric acid solution. The advantages in our quantitative method of working at room temperature and collecting the liberated iodine in another solvent are obvious. But in this case it was found by trial that dilute sulphuric acid must be used, instead of acetic acid, in order to prevent the formation of manganese dioxide, which interferes with the removal of the CCl_4 phase. Since the liberation of bromine cannot, therefore, be prevented by cutting down the hydrogen ion concentration to a very small value, it is important, as mentioned above, to avoid an excess of permanganate.

The addition of permanganate may be regarded as a titration; the "end point" described below in the procedure is easily determined and it is not difficult to avoid an excess of permanganate. This is possible because a solution of potassium iodide and carbon tetrachloride are both much better solvents for iodine than is pure water, so that, as the potassium iodide concentration becomes smaller, a larger proportion of the iodine passes into the carbon tetrachloride phase, and finally a colorless aqueous layer may be obtained.

The only sources of error in this method appear to be those which might arise from the addition of potassium permanganate in excess. If bromide is present, some bromine may be liberated. Also the addition of potassium permanganate in excess while considerable iodine is still present would result in the permanent formation of some iodic acid, the iodine of which would not be removed by the carbon tetrachloride. The tem-

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[1] Boettger, *Qualitative Analysis*, 2nd edit., page 387.

[2] Jannasch and Küster, *Z. physik. Chem.*, 28, 377 (1899).

porary formation of bromine or iodic acid during the earlier part of the operation does not, of course, introduce an error, for each reacts with the iodide still present, forming iodine. Although these errors may be easily avoided, it has seemed worth while to add a supplementary treatment with sulphurous acid by means of which the loss of an analysis may be avoided even if too much permanganate has been added.

Method of Analysis.

The following *materials* are required:

A glass-stoppered separating funnel of about 250 cc. capacity in which to carry out the oxidation of the iodide. The delivery tube should be cut off short and ground at an angle in order to facilitate washing after the discharge of the carbon tetrachloride solution of iodine.

A standard sodium thiosulphate solution, say 0.1 or 0.2 normal.

A potassium permanganate solution of about the same strength.

A freshly prepared 10 per cent. potassium iodide solution free from iodate.

Carbon tetrachloride free from oxidizing or reducting agents. A liter of carbon tetrachloride may be conveniently purified for use in these analyses by treating with iodine and dilute sulphuric acid for a few hours, shaking the mixture at intervals. The CCl_4 is drawn off from the acid solution by means of a large separating funnel, decolorized by shaking with a neutral sodium thiosulphate solution, and washed thoroughly by shaking with fresh portions of water.

Procedure.—Introduce into the separating funnel 25 to 30 cc. of carbon tetrachloride, 3 to 15 cc. sulphuric acid[1] (sp. gr. 1.20), and a definite amount of the potassium iodide solution to be analyzed. If bromide may be present, do not use more than 5 cc. of sulphuric acid and add 75 to 100 cc. water.

Add the permanganate solution from a burette, at the same time rotating the mixture, until the aqueous layer becomes very dark colored due to the liberated iodine; place the stopper in the separating funnel, shake vigorously, and let stand for at least half a minute. Carefully run the carbon tetrachloride solution of iodine into a glass stoppered flask containing about 25 cc. of 10 per cent. potassium iodide solution[2] and a few drops of acetic acid. Add a fresh portion of carbon tetrachloride and repeat the process until the aqueous layer is colorless.

As this stage is approached, add the permanganate solution drop by drop and shake the mixture after each addition. The decolorization of the permanganate and the liberation of iodine when the drop enters

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[1] Dilute nitric acid may be used instead of sulphuric, *e. g.*, when barium salts are present.

[2] A fairly concentrated potassium iodide solution is used to prevent the volatilization of iodine, and to aid in extracting the iodine from the carbon tetrachloride in the later titration with thiosulphate.

the solution can be easily observed. When the water layer appears colorless, withdraw as much as possible of the iodine by using successive small portions of carbon tetrachloride, add a drop of the permanganate, shake the mixture, and note the color of the aqueous and carbon tetrachloride layers. The end point has been reached (1) if the aqueous solution is pink colored owing to the presence of permanganate, and (2) if the carbon tetrachloride fails to show the pink color due to the presence of iodine.[1]

Titrate the liberated iodine with the standard sodium thiosulphate solution; shake the mixture continuously as the end-point is approached to ensure the rapid transfer of the iodine from the carbon tetrachloride to the potassium iodide solution.

In practice it is well to perform a preliminary titration to determine how much permanganate solution is required. The later analyses may then be quickly performed, since slightly less than this amount of potassium permanganate may be added before removing any iodine; but in this case, also, the mixture must be shaken vigorously at intervals.

If by accident an excess of permanganate be added while iodine is still present, and the formation of bromine or iodic acid be suspected, add a little sulphurous acid solution to again form the halide, and after 2 or 3 minutes treat with permanganate in the usual way.

The method was tested by means of a large number of analyses of potassium iodide solutions of known strength. The first group of analyses (Nos. 1–8) was made in connection with the investigation described in the following paper. The remaining analyses (Nos. 9–22) were made at a later date by one of us to supplement the first analyses and to determine the best conditions of analyzing iodide in the presence of chloride and bromide.

First Group of Test Analyses.

The carbon tetrachloride was not purified as directed in the procedure, and contained a trace of oxidizing material. In each of several blank analyses with approximately the same quantity of carbon tetrachloride as was used in an actual experiment, a slight amount of iodine was liberated which corresponded to about 0.06 cc. of the thiosulphate solution.

In the first analyses the sodium thiosulphate solution was 0.07348 normal. It was standardized: (1) by comparison with an iodine solution which had been titrated against arsenious oxide by the method described by Washburn[2] and (2) against a solution of copper sulphate by the method of Gooch and Heath,[3] the copper content of this solution

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[1] This second test of the end-point is valuable when bromide is present, for the permanganate color may then disappear, but the carbon tetrachloride becomes yellow, not pink.

[2] Washburn, THIS JOURNAL, **30**, 31 (1908).

[3] Gooch and Heath, *Z. anorg. Chem.*, **55**, 119 (1907); *Am. J. Sci.*, **24**, 65.

having first been determined by electrolysis. The results of the two methods agreed within 0.1 per cent., but it is doubtful if this accuracy could be claimed for the copper standardization. The concentration of the permanganate solution was not determined.

The potassium iodide solution was prepared by dissolving in 1 liter 15.00 grams of the pure, dry salt (Kahlbaum's guaranteed reagent). This solution was analyzed by measuring out three 100 cc. portions and precipitating the iodide as silver iodide. The precipitate was washed thoroughly with warm water by decantation, collected upon a weighed platinum Gooch filter, heated at 200° for 12 hours, and weighed. The three determinations gave for the normality of the solution,[1] 0.09054, 0.09052 and 0.09057—mean 0.9054. These results are concordant, and the mean is probably more nearly accurate than the value, 0.09030, derived from a single observation of the weight of salt taken.[2]

The results of the first eight analyses are given in Table I. The first five are with potassium iodide alone; in the preliminary analysis (No. 4 in the table) excess of permanganate was added while iodine was still present, and was reduced by the sulphurous acid treatment described in the procedure. In the remaining three analyses 25 cc. 0.1 formal copper sulphate solution were also added, which resulted in the precipitation of cuprous iodide and thus subjected the method to a very severe test. The sulphuric acid concentration was varied greatly in these experiments. In each case the burette reading given in the last column of the table has been diminished by 0.06 in accordance with the blank experiments described above. The initial volume (second column) refers to the total volume of the aqueous solution at the beginning of the experiment. All numbers are cubic centimeters.

TABLE I.—TITRATION OF 25.05 CC. KI SOLUTION WITH 0.07348 NORMAL $Na_2S_2O_3$.

No.	Initial volume.	H_2SO_4 (1.20).	$CuSO_4$ soln. 0.1 normal.	$KMnO_4$ soln. added.	$Na_2S_2O_3$ soln. (corrected).
1	75	2.5	..	15.4	30.80
2	75	25.0	..	15.4	30.82
3	75	25.0	..	15.4	30.85
4	75	25.0	..	15.6	30.86[3]
5	75	50.0	..	15.4	30.82
6	100	2.5	25	15.4	30.82
7	100	25.0	25	15.4	30.84
8	100	50.0	25	15.4	30.82

Mean, 30.82

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[1] International atomic weights of 1908 were used in connection with the first group of analyses (Nos. 1–8). In the remainder of the work 1910 atomic weights were used. The weights of salts were not corrected to vacuum.

[2] This difference of 0.27 per cent. might be due to the presence of sodium iodide in the potassium iodide reagent.

[3] Preliminary experiment, rejected in taking the mean.

The concentration of the potassium iodide solution calculated from the mean burette reading (30.82 cc.) is 0.09041 normal, which is only 0.14 per cent. less than the value, 0.09054, given by the gravimetric analyses. An examination of the individual analyses shows that the extreme variation from the mean is 0.1 per cent., and that the result is not affected by a 20-fold variation in the concentration of sulphuric acid, nor by the presence of copper sulphate.

Other analyses made at the same time as the above gave equally satisfactory results. For example, the 0.1 and the 0.01 normal potassium iodide solutions, which were used in the conductance measurements described in an earlier paper,[1] were analyzed by this method. Four titrations of the first solution and two of the second were made. The normality obtained in the first case was almost identical with, and that in the second one about 0.1 per cent. greater than, the value calculated from the weight of the pure dry salt.

Second Group of Test Analyses.

The carbon tetrachloride used in the following analyses was purified as described in the procedure, with the result that no iodine was liberated in blank analyses and the uncertain correction applied in the above experiments was eliminated.

Two different thiosulphate solutions were used, and the relation between them was determined several times by comparing both with the same solution of copper sulphate.

The stock thiosulphate solution was standardized during the following experiments by Dr. W. D. Harkins against pure iodine[2] and was found to be 0.09577 normal. The corresponding concentration of the second thiosulphate solution was 0.1074. The latter solution was used in analyses 9–18 (Table II).

The second method of standardization tried was the comparison of one of the thiosulphate solutions with a $KMnO_4$ solution which had been standardized by Mr. A. C. Melcher against sodium oxalate. The $KMnO_4$ was added to excess of KI in a dilute sulphuric or acetic acid solution. The results were concordant, but the normality calculated for the thiosulphate solution was 0.3 per cent. less than that derived from the iodine standard. It is shown in an appendix to this paper that one-third to one-half of this difference is due to the conditions under which the permanganate solution had been standardized. There still remains, however, a discrepancy of 0.15 to 0.2 per cent. between the two standardizations, and

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[1] Bray and MacKay, THIS JOURNAL, 32, 917 (1910).

[2] The iodine had been used in the experiments on the hydrolysis of iodine (Bray, THIS JOURNAL, 32, 932 (1910)) and thus was free from soluble impurities, including chlorine and bromine. This was twice sublimed, and dried over calcium chloride for several days.

it therefore seems improbable that the concentrations of the thiosulphate solutions derived from the iodine standard are too low.

In the third method of standardization, however, in which the thiosulphate solutions were referred to copper as standard by the method used in the first analyses, the normalities were found from numerous careful experiments to be 0.0960 and 0.10765, *i. e.*, over 0.2 per cent. greater than those given by the iodine standard. The conclusion was finally reached that the absolute accuracy of the copper standard is not quite as high as we had at first supposed.[1]

[1] Since this result differs from that found in the standardization of the thiosulphate used in the first group of test analyses, it has seemed worth while to give the details of the final experiments.

The copper sulphate used was prepared from the commercial salt by recrystallizing once from sulphuric acid solution and twice from water. The copper content of the copper sulphate solutions was determined from several concordant electrolytic analyses, in which the copper was deposited from a dilute nitric acid solution on a rotating cathode. The apparatus was kindly placed at our disposal by Dr. E. B. Spear. The deposition of copper was shown to be practically complete by evaporating the solution nearly to dryness and adding ammonia.

The above normalities were derived from a series of titrations of each thiosulphate solution against the pure copper sulphate solution according to the directions of Gooch and Heath, using 5 g. potassium iodide in the presence of acetic acid and not allowing the volume to exceed 100 cc. Contrary to the statement of these investigators, the results were found to be less satisfactory in dilute sulphuric or hydrochloric acid than in acetic acid solutions. In the latter case the amount of iodine liberated after the completion of the titration was negligible in half an hour, while in the presence of sulphuric or hydrochloric acid at concentrations less than those recommended by Gooch and Heath the iodine liberated in this time corresponded to over 0.10 cc. of 0.1 normal thiosulphate, and the reaction continued at this rate for several hours. This reaction is undoubtedly the oxidation of hydriodic acid by oxygen; it was catalyzed by light, and possibly by the presence of the finely divided cuprous iodide precipitate. In the acetic acid solution the titration could be made slowly, and this was a great advantage in determining the end point.

As the end point was approached the color due to the presence of starch slowly faded, but the particles of cuprous iodide retained a slight but distinct dark color when the color in the solution was very faint. The most clearly defined end point was the change of color of the suspended precipitate from this dark shade to the yellowish white of pure cuprous iodide. The dark color of the cuprous iodide in the presence of iodine and starch indicates that iodine is adsorbed or dissolved by the cuprous iodide. A possible explanation of the high thiosulphate concentration obtained in this standardization is that a trace of iodine is dissolved in the cuprous iodide and is not reduced by the thiosulphate.

In each titration from 30 to 40 cc. of thiosulphate were used, and the results were reproducible within 0.1 per cent. In the earlier experiments (in connection with the first group of analyses) a smaller volume was used, and the excess of thiosulphate added at the end point may have been a little greater than in the final experiments; both of these differences in treatment would lead to a relatively lower concentration for the thiosulphate in the first experiments.

Similar experiments were performed with a solution of commercial copper sulphate. (A small light-colored precipitate settled out in a few days and the clear solution was

The potassium iodide solution used in analyses Nos. 9–18 was prepared from the pure salt, which had been recrystallized from water. The crystals were heated for 16 hours at 150°, and 15.473 grams were dissolved and diluted to 1000.3 cc., at 25°, which corresponds to a normality of 0.09305. This value was thought to be a little high on account of the presence of a few particles of cork in the salt. Three 50 cc. portions (measured at 25°) were analyzed by Dr. W. D. Harkins by weighing silver iodide. To prevent occlusion of $AgNO_3$, the mixture was allowed to stand over night after the addition of slightly less than an equivalent amount of silver nitrate. The silver iodide precipitates were washed with cold water, and were heated 4 hours at 120° and 4 hours longer at 170°. The normalities found were 0.09285, 0.09292 and 0.09293; and the mean value, 0.09290, normal, was accepted as the concentration of the potassium iodide solution.

This solution was proved to be free from chloride by treating 100 cc. with permanganate according to the regular procedure to remove the iodide, heating the resulting solution with dilute nitric acid, filtering, and adding silver nitrate. Considerably less than 1 mg. of silver chloride was precipitated.

The results of the analyses of this solution are given in Table II. Chloride was present in Nos. 11 and 12, and bromide in Nos. 15–18. Blank experiments with potassium bromide alone under the conditions of analyses Nos. 15–18 showed that a drop of potassium permanganate was decolorized only very slowly in the dilute acid solutions (correspond- used in the experiments.) The thiosulphate concentrations were found to be slightly more than 0.1 per cent. greater than before. This difference disappeared or even changed sign when the $CuSO_4$ solution was treated with bromine, boiled long enough with dilute H_2SO_4 to expel the bromine, and then titrated in the usual way after adding excess of sodium acetate. It therefore seemed probable that the difference was due to the presence of a trace of ferrous sulphate or possibly of cuprous sulphate in the commercial copper sulphate.

TABLE II.—TITRATION OF 25.00 CC. KI SOLUTION WITH 0.1074 NORMAL $Na_2S_2O_3$.

No.	Initial volume.	H_2SO_4 (1.20).	KCl soln. 0.2 normal	KBr soln. 0.1 normal.	$KMnO_4$ soln. added.	$Na_2S_2O_3$ soln.
9	55	15	..	..	18.9	21.62
10	55	15	..	..	18.8+	21.62
11	55	15	10	..	18.85	21.63
12	55	15	10	..	18.85	21.62
13	55	2	..	..	18.84	21.62
14	110	5	..	..	18.82	21.62
15	110	2	..	10	18.82	21.62
16	115	3	..	10	18.8+	21.61
17	115	5	..	10	18.85	21.62
18	125	15	..	10	18.82	21.65
					Mean,	21.62

ing to Nos. 15–16) but almost immediately in the most concentrated acid (corresponding to No. 18). The same observations were made in the actual experiments at the end point of the permanganate titration.

The results are seen to be remarkably concordant, and to be independent of the acid concentration, the volume of the solution and the presence of chloride. Bromide does not affect the result, provided that the concentration of the sulphuric acid is not too large. From these analyses, and the blank experiments already mentioned with bromide alone, the limiting concentration of acid is placed at about 5 cc. sulphuric acid (1.20) in 100 cc. aqueous solution.

From the mean burette reading (21.62), and the thiosulphate concentration based on the iodine standard, the potassium iodide solution is calculated to be 0.0929 normal, which is in perfect agreement with the concentration derived from the gravimetric analyses. The proof of the absolute accuracy of the titration is not quite complete, since slightly greater concentrations are calculated for this potassium iodide solution from the weight of potassium iodide taken, and by using the copper standard for the thiosulphate solution; but the results render it extremely probable that the use of pure dry potassium iodide as an iodometric standard would yield results accurate to within 0.1 per cent. This method of standardizing thiosulphate solutions has the following advantages: the results are perfectly reproducible; and the method is direct, since the iodine titrated was originally present in the potassium iodide weighed out. Since the iodine standard also has these advantages, and the copper standard does not, the rejection of the copper standard seems justifiable.

The question next examined was the relation between the amounts of potassium permanganate and sodium thiosulphate solutions used in these analyses. Under the existing conditions the oxidation of iodide by permanganate is essentially a direct titration of the iodide by the permanganate. The end point is definite, and the amount of potassium permanganate used in each experiment seldom differed by more than 0.1 per cent. from the mean value, 18.83 cc. It therefore seemed that it might be possible to use the permanganate titration in analyzing the potassium iodide solution, and thus dispense with the final thiosulphate titration. But when the permanganate solution was compared directly with thiosulphate by adding the permanganate to an excess of potassium iodide in a dilute acid solution and titrating the liberated iodine, it was found that 18.83 cc. of the permanganate solution was equivalent to 21.73 cc. thiosulphate solution, instead of 21.62 cc. as expected. The difference 0.11 cc. is the error in the permanganate titration of iodide; and, since the error may depend upon the experimental conditions, it is evident that the permanganate titration could be used only as an empirical method, and might not be reliable, if the conditions were altered.

The reason for this error was found to be the incomplete reduction of permanganate to the manganous state when the iodide was not present in excess. The amount of oxidizing material present in the aqueous solution, after the permanganate titration had been completed and the iodine removed, was determined in No. 14 by adding a little potassium iodide to the aqueous solution in the separating funnel; the iodine liberated was equivalent to 0.09 cc. thiosulphate, while, judging from the color, the amount of permanganate present corresponded to only 0.01 cc. The number 0.09 is the error in the permanganate titration, and it is thus possible by this method to measure this error directly.

In the final experiments (Nos. 19–22) this direct method was used to determine the error in the permanganate titration. The amounts of thiosulphate solution used are given in the last column of Table III under the heading "$KMnO_4$ error;" the values in Nos. 19 and 20 are only approximate; the more accurate ones in Nos. 21 and 22 were derived from results obtained by using a dilute thiosulphate solution. The amount of thiosulphate solution equivalent to the mean amount (19.97 cc.) of permanganate solution was determined in the presence of excess of iodide to be 25.82 cc. On subtracting the experimentally determined value of the "$KMnO_4$ error," 0.10, the result, 25.72, is seen to agree almost exactly with the thiosulphate titration, 25.71 cc.

The results of all the experiments (Nos. 9–22) show that there is a 0.4–0.5 per cent. error in the direct titration of iodide by permanganate due to the incomplete reduction of permanganate to the manganous state. The possibility that this error is present in other permanganate titrations is considered in a note at the end of this article.

In the final experiments the stock 0.09577 normal, thiosulphate solution was used.

The potassium iodide solution was prepared from Merck's "neutral reagent," which contained chloride, by dissolving 16.614 grams of the dry salt and diluting to one liter. Three 50 cc. portions were analyzed by Dr. Harkins; the average weight of the silver iodide plus silver chloride precipitate was 1.793 grams. Two 50 cc. portions were analyzed for chloride, after removing the iodide by the regular procedure with permanganate; the mean weight of silver chloride was 0.0242 gram. The difference between 1.793 and 0.0242 gave the weight of silver iodide, from which the potassium iodide concentration was calculated to be 0.09840 normal. A similar correction of the weight of salt taken for the weight of potassium chloride present (corresponding to the amount of silver chloride found) led to the normality 0.09856. The result based on the weight of the silver salts is considered the more accurate; the difference of 0.16 is probably due to the presence of a trace of impurity other than chloride in the potassium iodide reagent.

The results are presented in the following table. The meaning of the results in the last column has already been explained.

TABLE III.—TITRATION OF 25.00 CC. OF A KI SOLUTION WITH 0.09577 NORMAL $Na_2S_2O_3$.

No.	Initial volume cc.	H_2SO_4 (1.20). cc.	$KMnO_4$ solution. cc.	$Na_2S_2O_3$ solution. $Na_2S_2O_3$ titration.	$Na_2S_2O_3$ solution. $KMnO_4$ error.
19	100	5	20.4	25.72	0.07
20	100	5	19.97	25.71	0.08
21	100	5	19.97	25.71	0.10
22	100	5	19.98	25.71	0.10

In experiment 19 a considerable excess of $KMnO_4$ was added while a large amount of iodine was still present, and the supplementary treatment with sulphurous acid was used. The fact that no error is introduced by this treatment is established by the accuracy of the final thiosulphate titration, 25.72 cc.

From the mean value of the thiosulphate titration the concentration of potassium iodide is calculated to be 0.09849, which is intermediate between the two values derived above from the weights of the silver and of the potassium salts, and does not differ from either by more than 0.1 per cent.

Summary.

In this article a method of determining iodide in aqueous solution has been described, which depends upon the oxidation of the iodide to iodine by permanganate, the removal of the liberated iodine by carbon tetrachloride, and the titration of this iodine with a standard sodium thiosulphate solution.

The test analyses (Tables I–III) with potassium iodide solutions of known concentrations show that the titration results are perfectly reproducible, and independent of the presence of chloride, bromide or copper sulphate.

From the standpoint of absolute accuracy this method is also satisfactory, since the results agreed within less than 0.1 per cent. with those based on iodine as standard. Pure, dry potassium iodide may therefore be recommended as an iodometric standard.

Two other iodometric standards yielded less satisfactory results. From a single series of experiments with a permanganate solution, standardized against sodium oxalate, the concentration of a stock sodium thiosulphate solution seemed to be about 0.15 per cent. too low; while from careful experiments with a copper sulphate solution, standardized by weighing electrolytically deposited copper, the concentration of the thiosulphate solution was found to be about 0.2 per cent. too high.

In the method of analysis here described the treatment with permanganate is essentially a direct titration of iodide by the permanganate. It is impossible, however, to replace the thiosulphate titration by this permanganate titration, since the reduction of permanganate to the manganous state was found to be not quite complete, and the resulting error corresponded to about 0.10 cc. (or 0.4–0.5 per cent.) of the permanganate solution. This error was measured directly by adding a little potassium iodide to the aqueous solution (after the removal of the carbon tetrachloride) and titrating the iodine then liberated.

BOSTON, July, 1910.

A SOURCE OF ERROR IN PERMANGANATE TITRATIONS; PRELIMINARY NOTE.

BY W. C. BRAY.

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In the direct titration of iodide by permanganate described in the preceding article, the permanganate was found to be incompletely reduced to the manganous state, and the resulting error was about 0.10 cc. of the 0.12 normal permanganate solution. It is therefore evident that in this reaction,

$$MnO_4^- + 5I^- + 8H^+ = Mn^{++} + 2^1/_2I_2 + 4H_2O,$$

the reduction of the permanganate takes place in stages, and that the final stage takes place more slowly than the reaction involving the disappearance of permanganate.[1]

Since the reduction of permanganate undoubtedly takes place in stages in other reactions, a similar error is possible in other permanganate titrations, and indeed is to be expected wherever the final stage of the reaction is known to take place relatively slowly. Apparently such a case is furnished by the titration with oxalic acid; for the kinetic experiments of Skrabal[2] have shown that the reduction from the manganic to the manganous state by oxalic acid is a slow reaction, and that a stable complex is formed between the manganic salt and oxalic acid.

Accordingly the following experiments (Table IV) were undertaken to determine under what conditions the error due to incomplete reduction of permanganate was appreciable in the oxalic acid titration. As in the previous experiments (Table III), this error was measured directly, by adding a little potassium iodide to the cold solution after the permanganate end point had been reached, and titrating the liberated iodine

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[1] That the incomplete reduction of the permanganate is due to an equilibrium involving iodine, such as $Mn^{+++} + I^- = Mn^{++} + {}^1/_2I_2$, seems improbable, since the concentration of the iodine is kept at a very small value by the presence of the carbon tetrachloride phase.

[2] Skrabal, *Z. anorg. Chem.*, 42, 1 (1904).