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.

Received July 25, 1910.

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).

with thiosulphate. A dilute thiosulphate solution was used and the corresponding volume of the permanganate solution is recorded in the last column of the table.[1] This result includes the "blank" correction due to the excess of permanganate added to produce the end point, which from the color was estimated not to exceed 0.01 cc. in Nos. 1 and 2, in which the volume was small, and 0.02 cc. in the remaining experiments.

In each experiment (except No. 8) a 25 cc. portion of pure sodium oxalate solution was mixed with a known amount of sulphuric acid; the mixture after dilution to the volume given in the table was heated to 90°, and the permanganate solution was added from a burette. In the last four experiments, after about 80 per cent. of the oxalate had been oxidized, the mixtures were cooled, and the titration completed at about 25°. In all cases the end point was approached very carefully, and the last drops were added slowly. In experiments 1–4 the end point was sharply defined; in Nos. 5–8 the pink color seemed to fade very slowly, but no extra permanganate was added. In Nos. 9 and 10, however, when the acid concentration was very large, the first pink color faded quickly and more permanganate was added; and at the low temperatures the end point was even less definite, especially at the large acid concentrations (Nos. 13 and 14). In experiments 2, 3, 4, and 11 the solution became slightly brown during addition of permanganate, but on standing this color disappeared, rapidly at the high temperature and slowly at the low.

Table IV.—Titration of Sodium Oxalate with 0.1 Normal $KMnO_4$.

Expt. No.	Oxalate solution. cc.	H_2SO_4 (1 20). cc.	Initial volume. cc.	Final temp. about	$KMnO_4$ solution, 0.12 *N*. Titration. cc.	$KMnO_4$ solution, 0.12 *N*. Error. cc.
1	25	10	50	80°	21.20	0.02
2	25	10	300	80	21.23	0.03
3–4	25	10	300	80	...	0.03
5	25	50	300	80	21.26	0.05
6–7	25	50	300	80	...	0.05
8	75	50	300	70	...	0.06
9	25	250	300	80	21.26	0.07
10	25	250	300	80	...	0.06
11	25	10	50	25	21.29	0.07
12	25	10	300	25	21.27	0.06
13	25	50	300	25	21.32	0.11
14	25	250	300	25	21.35	0.14

From an examination of the table it is seen that when the amounts of permanganate solution used are diminished by the numbers in the last column, the values are nearly constant, with a mean value 21.20. It is

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[1] It was shown that the liberation of iodine in the concentrated acid solutions was not due to the action of oxygen on hydriodic acid by allowing the mixtures to stand for half an hour after the titration and determining the amount of iodine liberated in that time.

obvious that this is the amount of permanganate actually equivalent to 25 cc. of the oxalate solution, and that the numbers in the last column show the errors under different experimental conditions.

On deducting the blank experiment correction, the error in the first four experiments, due to the incomplete reduction of the permanganate, is seen to be only 0.01 cc., which is negligible when the amount of permanganate used is sufficiently large. The most favorable conditions for the titration, therefore, are a small amount of acid and a final temperature of 70 or 80°. Since these conditions are those recommended in books on quantitative analysis[1] it is evident that the error due to the incomplete oxidation of permanganate need not ordinarily be taken into account.

The large errors in the remaining experiments show the importance of avoiding the following unfavorable conditions in titrating: low temperature, high acid concentration and large volume. In the last experiment, for example, the error was 0.14 cc. of which only 0.02 was due to permanganate alone.

A comparison of experiments 6 and 8 shows that the absolute error remained nearly constant (and the percentage error decreased greatly) when the concentration of manganous salt was increased threefold. This result was confirmed by a pair of experiments, in one of which a large excess of manganous sulphate was added initially. In the standardization of permanganate referred to in the preceding paper the titrations were made under the same conditions as in experiments 6–8, the volume of permanganate varied between 40 and 60 cc., and no blank correction was applied for the excess of permanganate. It follows therefore, as already pointed out, that the error in this standardization was 0.10–0.15 per cent.

From the present results it is evident that an error due to incomplete reduction of permanganate is possible in titrating other reducing agents, and that each case must therefore be carefully investigated if an accuracy of 0.1 per cent. is desired. In many instances, however, the above direct method cannot be used in determining the error. For example, in the ferrous sulphate titration the ferric sulphate formed would itself cause the liberation of iodine. In such cases the constancy of the results under widely different conditions of temperature and acid concentration would probably insure the accuracy of the method of titration. This conclusion would also be confirmed if in an investigation of the reduction of a manganic salt by the reducing agent, as ferrous sulphate, it were found that the reaction takes place rapidly and completely.

These experiments will not be continued by the author at the present time, but the question whether there is an appreciable error in the ferrous

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[1] Treadwell, "Hall's Translation, II, 379, recommends a temperature of 70°, 10 cc. H_2SO_4, and a volume of 200 cc

sulphate titration will doubtless be settled in the near future by the investigation of the oxalate and ferrous sulphate titrations now in progress at the Bureau of Standards. The author takes pleasure in thanking Dr. W. F. Hillebrand and Mr. R. S. McBride, of the Bureau of Standards, for their kindness in reading and criticizing this note before its publication.

Boston, July, 1910.

[Contributions from the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology, No. 55.]

THE EQUILIBRIUM BETWEEN SOLID CUPROUS IODIDE AND AQUEOUS SOLUTIONS CONTAINING CUPRIC SALT AND IODINE.

By W. C. Bray and G. M. J. MacKay.

Received July 25, 1910.

This investigation was originally undertaken in order to test the generally accepted view that the cuprous ion is monatomic (Cu^+), rather than diatomic (Cu_2^{++}), and especially to check the results of Bodländer and Storbeck[1] on this subject. The work, however, was interrupted two years ago and has not been continued; the results then obtained are presented in the present article as an investigation of the law of mass action in dilute aqueous solutions.

Cuprous iodide is difficultly soluble in water, but in the presence of iodine a considerable amount dissolves, owing to the formation of cupric iodide and tri-iodide. The following two equilibria are involved:

$$CuI \text{ (solid)} + \tfrac{1}{2}I_2 = Cu^{++} + 2I^-, \text{ and } I_3^- = I_2 + I^-.$$

From the experimental results at 25° presented below, values have been determined, under widely different conditions, for the two equilibrium functions:

$$(Cu^{++})(I^-)^2/(I_2)^{\frac{1}{2}} = K', \text{ and } (I^-)(I_2)/(I_3^-) = K.$$

Bodländer and Storbeck have reported a single, apparently not very accurate experiment at room temperature (18–20°), in which 1 liter of solution saturated with both cuprous iodide and iodine was found to contain 0.01666 gram molecule of cupric salt, and 0.00946 equivalent of dissolved iodine.

The *cuprous iodide* was prepared according to the directions of Bevan Lean,[2] by adding one formula weight of potassium iodide dissolved in 150 cc. of water to a solution of one formula weight of copper sulphate dissolved in 1500 cc. of water saturated with sulphur dioxide. The resulting precipitate was washed several times with water containing sulphur dioxide, and finally with pure water until all trace of sulphate

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[1] Borländer and Storbeck, *Z. anorg. Chem.*, **31**, 469 (1902).

[2] *J. Chem. Soc.*, **73**, 149 (1898).