# THE STANDARDIZATION OF POTASSIUM PERMANGANATE SOLUTION BY SODIUM OXALATE.[1]

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Received February 7, 1912.

## I. Introduction.

*1. Object of the Research.*—The standardization of potassium permanganate solutions has been the subject of much study and an excessive amount of controversy. There have been far too many standards proposed for this work to permit one not familiar with the subject to select the best; and, in fact, it is doubtful whether or not any one of those standards proposed can in all senses be considered the best. However, the work of the Bureau of Standards has demanded that some substance be selected for this use, which could be employed with a certainty of a reasonably correct result. It was desired, if possible, that the standard selected should serve a threefold purpose, *viz.*, first, as a primary standard of oxidimetry; second, as a working standard for regular use in our own laboratories; and third, as a substance which could be distributed by the Bureau with a guarantee both as to its purity and as to its reducing value when used under specified conditions.

Although the voluminous literature relating to the standardization of potassium permanganate solutions has been examined with considerable care, it is not thought desirable to give a history of the subject, or even a bibliography. None of the theories considered here are new; but it is hoped that the experimental facts presented will be of value as a guide to the proper use of sodium oxalate as a standard.

*2. Considerations Affecting the Choice of a Standard.*—It is seldom that a single measure can be used both as a primary reference standard and as a regular working standard; but for some volumetric work this is possible. To serve any such double function, a substance must meet the following conditions:

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[1] Published by permission of the Director of the Bureau of Standards.

(*a*) There must be reasonable ease of preparation and accurate reproducibility.

(*b*) The purity must be determinable with sufficient accuracy; and the purified material must be stable under ordinary conditions of the laboratory.

(*c*) The use of the material in regular work must demand neither complex apparatus nor difficult manipulations.

(*d*) Such precision must be obtainable when it is used with ordinary care that one, or at the most a very few determinations suffice for the fixing of the value of a standard solution.

(*e*) The accuracy obtained under ordinary conditions of its use in standardization must be at least as great as that required in the use of the solution to be standardized.

*3. Reasons for the Choice of Sodium Oxalate.*—In the above five respects, it appeared that sodium oxalate was probably best suited to our needs; and a detailed study of this standard was undertaken.

The methods of preparation and testing of sodium oxalate have been carefully studied by Sörensen.[1] In continuation of such study, Mr. J. B. Tuttle and Dr. Wm. Blum, of this laboratory, have carried out several important lines of work; and at the request of the Bureau of Standards, several firms of manufacturing chemists have improved their methods of preparation of sodium oxalate on a large scale. At this point it is sufficient to state that all of this work indicates that it can be prepared in a suitable form at reasonable expense; that it is reproducible; that its purity can be tested readily; and that once purified, it is satisfactorily stable under ordinary conditions.[2]

The discussion of the other three criteria as to the value of sodium oxalate, *viz.*, convenience, precision and accuracy, forms the subject of the present article.

In advance of the general discussion it is not amiss to state the conclusions drawn as to these three points. It appears that, when the conditions for the use of the sodium oxalate have been defined, they may be conformed to easily and no unusual apparatus or complex procedure is necessary. The accuracy obtainable is, within the limits of our present knowledge, sufficient for even the most refined work (see p. 415); and the precision or agreement of duplicates is satisfactory.

Along with such striking advantages we find certain disadvantages, but none of these appear serious. The more important are as follows:

(*a*) The largest sample which can be used ordinarily (for 50 cc. of 0.1 *N* $KMnO_4$) is only 0.3 gram. This necessitates an accurate weighing in order to gain a high degree of accuracy. It is not desirable to use a stand-

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[1] *Z. anal. Chem.*, **36**, 639; **42**, 333 and 512.

[2] See Blum, THIS JOURNAL, **34**, 123 (1912).

ard stock solution, unless freshly prepared. If such solution is kept for any considerable length of time, it acts upon the glass of its container; it is also slowly decomposed by the action of light.

(*b*) The detection of small amounts of allied organic compounds in the sodium oxalate is rather difficult, except by comparison of the reducing value with that of other samples of known purity.

(*c*) The initial drying of the oxalate is subject to slight uncertainty; but once dried it is practically non-hygroscopic.

4. *Normal Course of the Reaction.*—In 1866 Harcourt and Esson[1] concluded from a study of the speeds of reaction under various conditions, that the steps of the reaction are as follows:

I. $2Mn(OH)_7 + 5H_2C_2O_4 = 2Mn(OH)_2 + 10CO_2 + 10H_2O$ (very slow).
II. $3Mn(OH)_2 + 2Mn(OH)_7 = 5Mn(OH)_4$ (very fast).
III. $Mn(OH)_4 + H_2C_2O_4 = Mn(OH)_2 + 2CO_2 + 2H_2O$ (fast, but less so than II).

Among the more recent articles presenting either experimental or theoretical evidence on this subject, the more important are those by Schillow[2] and by Skrabal.[3]

From measurements of the speeds of reaction, the former presents the following system as representing the steps of the reaction:

I. $Mn(OH)_7 + 2H_2C_2O_4 = Mn(OH)_3 + 4CO_2 + 4H_2O$ (very slow).
II. $Mn(OH)_3 \cdot 2H_2C_2O_4 + Mn(OH)_7 = 2Mn(OH)_3 + 4CO_2 + 4H_2O$ (measured).
III. $Mn(OH)_3 + 2H_2C_2O_4 = Mn(OH)_3 \cdot 2H_2C_2O_4$ (practically instantaneous).

The second of these can be divided into two parts:

II*a*. $Mn(OH)_3 \cdot 2H_2C_2O_4 + Mn(OH)_7 = Mn(OH)_6 + Mn(OH)_4 \cdot 2H_2C_2O_4$ (measured).
II*b*. $Mn(OH)_4 \cdot 2H_2C_2O_4 + Mn(OH)_6 = Mn(OH)_3 + 4CO_2 + 4H_2O$ (practically instantaneous).

However, this author qualifies the proposed explanation by the following statements:

"This scheme is considered only as an approximate picture of the phenomenon and is true particularly for mean concentration of hydrogen ions and low temperatures (0–25°). Under other conditions, side reactions and disturbances enter in, which can be partially observed or foreseen..............

"In addition to the reactions given above, the following two also require consideration:

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[1] *Phil. Trans.*, **156**, 193.

[2] *Ber.*, **36**, 2735 (1903).

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

"IV. $2Mn(OH)_3 + H_2C_2O_4 = 2Mn(OH)_2 + 2CO_2 + 2H_2O$.

"V. $4Mn(OH)_2 + Mn(OH)_7 = 5Mn(OH)_3$."

These last reactions, however, are not assigned a definit role in the general scheme.

After an extended series of experiments on the speed of the reaction under various conditions, Skrabal[1] advances the following scheme as representing the course of the reaction:

Incubation period:

(1) $H_2C_2O_4 + KMnO_4 = Mn\cdots + CO_2$ (measurable).

(2) $H_2C_2O_4 + Mn\cdots = Mn(OH)_2 + CO_2$ (practically instantaneous).

Induction period:

(3) $Mn(OH)_2 + KMnO_4 = Mn\cdots$ (less rapidly).

(4) $Mn\cdots + H_2C_2O_4 = Mn(OH)_2 + CO_2$ (practically instantaneous).

(5) $Mn\cdots + H_2C_2O_4 = Mn(OH)_3{\cdot}H_2C_2O_4$ (practically instantaneous).

(6) $Mn\cdots = Mn(OH)_2 + Mn(OH)_4$ (practically instantaneous).

End period:

$$\text{I.}\begin{cases}(7)\ Mn(OH)_3{\cdot}H_2C_2O_4 = Mn\cdots\ \text{(measurable).}\\ (8)\ H_2C_2O_4 + Mn\cdots = Mn(OH)_2 + CO_2\ \text{(practically instantaneous).}\end{cases}$$

$$\text{II.}\begin{cases}(9)\ Mn(OH)_2 + Mn(OH)_4 = Mn\cdots\ \text{(less rapidly).}\\ (10)\ H_2C_2O_4 + Mn\cdots = Mn(OH)_2 + CO_2\ \text{(practically instantaneous).}\end{cases}$$

Since this last system of reactions is based upon elaborate experimental work it can be accepted as probably best representing the normal course of the reaction. For the present considerations any one of the systems would serve equally well to explain the observed facts.

The variations from a normal course will be considered after the experimental part of the present work has been described.

## II. Experimental Work.

*1. Reagents Employed.*—The water and sulfuric acid employed were frequently tested for reducing matter, and in each case were shown to be free from appreciable amounts of such impurities. The manganous sulfate was similarly tested for reducing and oxidizing influence and shown to be satisfactory. To purify the air used for the tests of Tables VI and VII, it was passed through cotton wool to remove dust and grease, bubbled through a solution of potassium hydroxide to take out any acid vapors present and then through solutions of chromic acid and potassium permanganate. The purified air had no detectable reducing effect upon dilute solutions of permanganate under the conditions of titration.

The carbon dioxide used for the tests of Table VI was taken from a cylinder of the commercial liquid and passed through water, chromic acid and permanganate solution before use. An analysis showed the

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[1] *Loc. cit.*

presence of about 3% of methane; but this gas seemed to have only a very slight reducing action on the permanganate in dilute solution, so that the results of the series in which it was used can be regarded as but slightly less reliable than the series in Table VII. For this latter group of tests, pure carbon dioxide was made from acid and sodium carbonate. This source gave a gas which had no detectable reducing action under the conditions of its use.

The potassium permanganate used for most of the work was a sample of good quality which had been made up in normal solution for over six months before filtration and dilution to tenth-normal strength for use. The diluted solution was filtered frequently through asbestos to ensure freedom from precipitated manganese dioxide. For the series of tests reported in Table IV*b*, a second permanganate was used. In this case the strong solution was boiled for a few minutes, cooled, filtered and diluted to tenth-normal strength. For the series of Table VII, still a different permanganate was employed, this stock being prepared in the same manner as the main solution. About 40 grams of solution were used for each titration.

The sodium oxalate used for all of the experiments except those of Table IV*b* was a sample specially purified in this laboratory by Mr. J. B. Tuttle. It is sufficient to state here that all tests indicated a total impurity of not over 0.05%. For the tests of Table IV*b*, another sample of sodium oxalate made by the Mallinckrodt Chemical Works, especially for our use, was employed. This material was shown by test to be as pure as that prepared in our own laboratory.

2. *Weighing of Oxalate and Permanganate Used.*—Since in all of the work described in the following part of this article only comparative values were required, the absolute amount of oxalate employed in any one test was not of importance, as long as the relative amounts present in the experiments of a series were accurately known. Therefore it was found desirable to use about a 20-gram portion of a 0.2 $N$ stock solution of the oxalate for each test. Each such sample was weighed from a buret to the nearest 5 mg.; the relative weight of each sample was thus determined to better than one part in 3000, in less time and with greater certainty than would have been possible by weighing out the dried powder.

In order to prevent any change in the strength of the stock solution from affecting the conclusions drawn from the results of any series of titrations, only those values obtained during a period of a few days are compared with each other. This plan avoided any uncertainty due either to slow decomposition of the oxalate in solution, occurring through action on the glass of the container or oxidation by the air through the aid of light, or to change in oxidizing value of the permanganate solution employed.

The measurement of the permanganate solution was accomplished by the use of a weight buret. For this work, this form of instrument possesses the following advantages: (*a*) Correction for the temperature changes which affect the volume of the solution, is not necessary; (*b*) completeness or uniformity of running down of the solution from the buret walls, is unessential; and (*c*) the solution can be weighed readily to 0.01 g. (1 part in 5000 on a 50 g. sample), whereas measurement to 0.01 cc. is exceedingly uncertain. The freedom from errors due to temperature changes is of great importance in this work, as the buret is often very appreciably warmed by the steam rising from the hot liquid undergoing titration.

The buret used was made from a 50 cc. cylindrical separatory funnel by drawing down the stem to the form of an ordinary buret tip. For exact work it has been found desirable to have this tip so drawn down that it will deliver about 10 cc. per minute or 0.03 cc. per drop.

*3. Effect of Conditions upon the Result of a Titration.*—The ordinary procedure for the use of sodium oxalate in the standardization of potassium permanganate is as follows: Dissolve about a quarter of a gram of the oxalate in 250 cc. of water, acidify with sulfuric acid, warm to 70° and titrate to the first permanent pink.

It was desirable to determin the effect of the variation of the following conditions upon the result obtained, *viz.*, temperature, acidity, volume of solution, rate of addition of the permanganate, access of air, presence of added manganous sulfate and, in connection with these, the corrections necessary upon the apparent end points. In order to accomplish such determinations, the factors were varied one at a time, noting the difference, if any, produced upon the apparent value of the permanganate. The results of the titrations are reported as the ratios of the oxalate used to the permanganate used multiplied by $10^{-2}$. These values are proportional to, and, indeed, numerically almost equal to, the iron value of the permanganate. Therefore, for purposes of discussion the values are treated as if they were the iron value of the permanganate, expressed in grams of iron per gram of solution. It should be noted that an increase in the iron value represents a decrease in the permanganate consumed, and *vice versa.* A variation of 0.01 cc. in the amount of permanganate used in a titration is approximately equivalent to a change of one unit in the last expressed figure of the iron value.

*a. End-point Corrections.*—In a recent article Dr. W. C. Bray[1] has suggested the necessity for the correction of the apparent end-point obtained in the reaction of oxalic acid and permanganate, and has recommended that the correction be determined as follows: After reaching the end-point, the solution is cooled to room temperature, potassium iodide

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[1] THIS JOURNAL, **32**, 1204 (1910).

solution is added, and the iodine liberated is at once titrated with dilute (0.02 *N*) sodium thiosulfate.

In order to test the necessity and the accuracy of this method under the various conditions of titration, we examined experimentally the following points:

(*a*) Does the equivalent in oxidizing power of the permanganate excess remain in the solution long enough to allow the necessary cooling before the titration with thiosulfate?

(*b*) Does the thiosulfate titration give the total permanganate excess used to produce the end point, or does it indicate only the permanganate which remains in the solution as such?

(*c*) Does the depth of the pink color at the end of the titration show how great an excess of permanganate has been added in order to produce that end-point?

Before applying the method of correction proposed by Bray, it is necessary to cool the solution to room temperature. Therefore, if, as is desirable, the permanganate end-point is obtained while the solution is hot, some time must elapse during cooling and it is possible that a loss of oxidizing (or iodine liberating) power would occur, which loss would render the correction as subsequently determined valueless. This point was tested by determining the residual oxidizing power of solutions to which had been added known amounts of permanganate at various temperatures (30–90°), with varying acidities (2–10% by volume $H_2SO_4$) and with the addition of various amounts of manganous sulfate (up to 1 g. $MnSO_4$ $4H_2O$). These experiments showed that no appreciable loss occurred within a period of one-half hour, if only a small amount of permanganate (0.02–0.20 cc. of 0.1 *N* soln.) is added to any such solution. Moreover, this condition was found to exist even when the permanganate was wholly decolorized by reaction with the manganous salt. The full oxidizing power was then retained in the solution, probably in the tri- or tetravalent manganese salts ($Mn^{\cdot\cdot\cdot}$ or $Mn^{\cdot\cdot\cdot\cdot}$). The lapse of 5–10 minutes necessary for cooling the solution to room temperature is thus shown to be without influence; and it is evident that the procedure described determines not only the permanganate remaining in the solution as such, but also that which was not completely reduced to the manganous condition.

The procedure described by Bray has been accepted on the above basis as giving a determination of the real excess of permanganate which was added to produce the end point. However, the question as to the difference between this end point correction and that determined by the depth of the pink color at the end point must be considered on a different basis.

For each of the titrations made in this investigation, two values were obtained, the one using the color method, the other the iodine method for correction of the total permanganate added. In several of the tables below both of these values are reported. By inspection of these data (Tables II, III and V) it will be apparent that, in general, the color correction and the iodine correction differ by no more than 0.02 cc., except when the end-point was reached with the solution at temperatures below 35°, or when the permanganate solution was added rapidly just at the end-point. This was true in all but six of over two hundred tests; and even in these, the difference between the two corrections was not more than 0.04 cc. It is, therefore, certain that if the end-point is approached slowly in a solution above 60° the depth of color will be proportional to the total excess of permanganate added, *i. e.*, no permanganate will be decolorized without at the same time being completely reduced to the manganous condition. However, at lower temperatures, in the presence of much sulfuric acid (more than 5% by volume), and particularly with rapid addition of permanganate or with insufficient stirring just preceding the end-point, the amount of permanganate decolorized but not wholly reduced to the manganous condition may easily be as much as 0.1 cc.

*b. Rate of Addition of the Permanganate.*—The rate of addition of the permanganate solution in the titration of iron in solutions containing chlorides has been shown to have considerable effect upon the result obtained.[1] The influence of this factor upon the oxalate-permanganate reaction was, therefore, studied.

The influence of varying the amount of permanganate added before the quick color changes of rapid reduction began was first tested. This factor has an influence only at low temperatures (below 40–50°) as at any higher temperature the reduction proceeds rapidly from the very start. Tests made at 30° in 5% sulfuric acid solution gave results as follows:

| Amount of $KMnO_4$ added before rapid decolorization was evident.............. | 3.0 cc. | 10.0 cc. | 25.0 cc. | 40.0 cc. |
|---|---|---|---|---|
| Results obtained (strength of $KMnO_4$).................. | 0.005936 | 0.005936 | 0.005932 | 0.005929 |
| | 37 | 35 | 33 | |
| | 34 | 37 | | |

These results show that the addition of a large amount of permanganate before rapid oxidation of the oxalate begins tends to give lower values for the permanganate solution, *i. e.*, to cause a larger consumption of permanganate. The influence of this factor is small, but it is of some significance, as will be apparent from the later discussion.

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[1] Skabarl, A., *Z. anal. Chem.*, **42**, 359 (1903). Friend, A. N., *J. Chem. Soc.*, **95**, 1228 (1909). Jones and Jeffrey, *Analyst*, **34**, 306 (1909).

After the initial reduction of 3–10 cc. of permanganate the rate of addition of the main portion of the permanganate was varied, giving the results listed in Table I. These experiments indicate that except on long standing at a high temperature (after starting the reaction), or with a very rapid addition of permanganate to a weakly acid solution at a high temperature, the rate of the addition of the permanganate during the main part of the titration has no influence. The high values obtained in experiments marked * are probably due to oxidation of the oxalic acid by the air; and the low values of experiments marked † show a loss of oxygen, because of the excessive rate of the permanganate addition.

TABLE I.—EFFECT OF RATE OF ADDITION OF PERMANGANATE DURING MAIN PART OF TITRATION.

| Acidity. vol. % $H_2SO_4$. | Temp. | Time for titration. min. | Result. corrected iron value. | Acidity. vol. %. $H_2SO_4$. | Temp. | Time for titration. min. | Result. corrected iron value. |
|---|---|---|---|---|---|---|---|
| 5 | 80° | 5 | 0.005945 | 2 | 30° | 0.5 | 0.005592 |
| | | 5 | 45 | | | 0.5 | 92 |
| | | 27[1] | 46 | | | 5.0 | 92 |
| | | 120[2] | 56* | | | 4.0 | 93 |
| | | 120[2] | 56* | | | 5.0 | 91 |
| | | | | | | 60[1] | 94 |
| | | | | | | 60[1] | 95 |
| 5 | 30° | 7 | 0.005942 | 2 | 90° | 0.5 | 0.005589† |
| | | 6 | 42 | | | 0.5 | 88† |
| | | 37[1] | 44 | | | 5 | 98 |
| | | 120[2] | 44 | | | 5 | 5600 |
| | | | | | | 30[1] | 00 |
| | | | | | | 30[1] | 5598 |

The effect of the rate of the addition of the permanganate just at the end-point has already been suggested (p. 400); but the following data will make this point clearer. In each pair of tests the only variable was the rate of the addition of the permanganate solution just before the end-point. Only the two experiments in each group may be compared (see Table II).

In the first part of Table II some rather extreme cases (experiments done at 30°) have been chosen to show how large the error of the apparent end-point may be, without any influence upon the corrected value. In cases where much smaller corrections were necessary (temperature 60° and above), the agreement of uncorrected values was better, regardless of the speed at which the end point was approached. The latter part of Table II shows this agreement of the uncorrected values at the higher temperature. Nevertheless, it is not desirable to approach the end-point so rapidly as to make a correction larger than 0.1 cc. necessary.

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[1] Dropwise, with stirring.

[2] Intermittent, without continuous stirring.

TABLE II.—EFFECT OF RATE OF ADDITION OF PERMANGANATE AT THE END-POINT.

In the first of each pair of experiments, the end-point was approached slowly, in the second rapidly.

| Temp. | Acidity. vol. % $H_2SO_4$. | Color blank. | Iodine blank. | Value of permanganate. | | |
|---|---|---|---|---|---|---|
| | | | | Uncorr. | Color corr. | Iodine corr. |
| 30° | 2 | 0.01 | 0.03 | 0.005584 | 0.005586 | 0.005589 |
| | | 0.25 | 0.34 | 37 | 71 | 87 |
| 30 | 5 | 0.03 | 0.09 | 0.005929 | 0.005933 | 0.005942 |
| | | 0.15 | 0.39 | 5894 | 12 | 42 |
| 30 | 5 | 0.05 | 0.085 | 0.005030 | 0.005034 | 0.005037 |
| | | 0.08 | 0.19 | 17 | 26 | 38 |
| 30 | 5 | 0.04 | 0.08 | 0.005923 | 0.005929 | 0.005935 |
| | | .... | 0.51 | 5871 | .. | 37 |
| 30 | 10 | 0.06 | 0.11 | 0.005636 | 0.005642 | 0.005648 |
| | | 0.08 | 0.14 | 33 | 43 | 50 |
| 60 | 2 | 0.05 | 0.05 | 0.005642 | 0.005649 | 0.005649 |
| | | 0.03 | 0.05 | 45 | 49 | 51 |
| 60 | 5 | 0.05 | 0.07 | 0.005638 | 0.005646 | 0.005649 |
| | | 0.05 | 0.06 | 40 | 44 | 46 |
| 83 | 2 | 0.06 | 0.07 | 0.005642 | 0.005650 | 0.005651 |
| | | 0.06 | 0.06 | 45 | 52 | 52 |
| 96 | 2 | 0.05 | 0.04 | 0.005647 | 0.005652 | 0.005651 |
| | | 0.2 | 0.15 | 33 | 61 | 54 |

*c. Volume of the Solution.*—The volume of the solution in which the titration is made might affect the rate of the reaction and, therefore, possibly the result of the titration. Tests were made of this point by varying the initial volume in a series of titrations made at 90° in solutions containing 5% by volume of sulfuric acid. The results were as follows:

| Initial volume.. | 50 cc. | 250 cc. | 500 cc. | 700 cc. | 1000 cc. |
|---|---|---|---|---|---|
| Values obtained | 0.005139 | 0.005139 | 0.005136 | 0.005133 | 0.005127 |
| | 36 | 39 | 34 | 32 | 29 |
| | | 37 | | | |

By increasing the initial volume beyond 250 cc., the resulting value for the permanganate solution is markedly decreased. That this is due to the change in the initial concentration of the oxalate is indicated by the results obtained in two titrations in which the initial volume was 1000 cc. but the amount of oxalate used was increased threefold, thus making its initial concentration about that ordinarily resulting in an initial volume of 350 cc. The results thus obtained were 0.005136 and 0.005136.

At 30° the initial rate of the permanganate reduction is so much less than at 90°, that it is not possible to note the effect of initial volume free from this influence. A few results were obtained as follows:

| Initial volume.................. | 50 cc. | 250 cc. | 1000 cc. |
|---|---|---|---|
| Values obtained................. | 0.005943 | 0.005942 | 0.005945 |
| | 45 | 42 | |

In these experiments no decided effect of volume is to be found.

It should be noted that in each of these cases the change in volume had no effect upon the concentration of the sulfuric acid present.

*d. Acidity and Temperature.*—The effects of acidity and of temperature were investigated by two series of experiments, the results of which are given in Tables III and IV. These data show that either higher temperature or less concentration of sulfuric acid tends to give higher values for the permanganate, *i. e.*, to reduce the amount of permanganate required. These effects are not large and, indeed, the results obtained in some cases show duplicates as discordant as experiments carried out under somewhat different conditions; nevertheless, the tendency in the two directions is rather convincing that these factors have a real influence upon the results obtained. The importance of even such slight variations is considerable, as will be apparent from the discussion later.

It will be seen from the data of Table IV that the first series exhibits a larger apparent influence of temperature than the second series reported. This is due to the greater care exercised in the latter series to stir the solution very vigorously and to add the permanganate more slowly, particularly at the beginning and end of each titration. However, the first series shows better the variation which may be expected if only ordinary titration precautions are observed.

TABLE III.—EFFECT OF ACIDITY AND TEMPERATURE.

| Temp. | Acidity. vol. % $H_2SO_4$. | Color blank. | Iodine blank. | Value of permanganate. | | |
|---|---|---|---|---|---|---|
| | | | | Uncorr. | Color corr. | Iodine corr. |
| 30° | 2 | 0.04 | 0.06 | 0.005129 | 0.005135 | 0.005137 |
| | 2 | 0.04 | 0.05 | 33 | 38 | 39 |
| | 5 | 0.04 | 0.05 | 27 | 32 | 34 |
| | 5 | 0.03 | 0.035 | 27 | 31 | 31 |
| | 10 | 0.05 | 0.10 | 18 | 25 | 32 |
| | 10 | 0.02 | 0.09 | 21 | 24 | 33 |
| 45 | 2 | 0.02 | 0.03 | 0.005134 | 0.005136 | 0.005138 |
| | 2 | 0.03 | 0.04 | 34 | 38 | 40 |
| | 5 | 0.03 | 0.04 | 30 | 34 | 35 |
| | 5 | 0.03 | 0.025 | 30 | 37 | 36 |
| | 10 | 0.01 | 0.03 | 35 | 36 | 39 |
| | 10 | 0.03 | 0.03 | 31 | 35 | 35 |
| | 10 | 0.02 | 0.035 | 37 | 40 | 42 |
| 60 | 2 | 0.02 | 0.02 | 0.005129 | 0.005132 | 0.005132 |
| | 2 | 0.03 | 0.03 | 36 | 40 | 40 |
| | 2 | 0.035 | 0.035 | 33 | 37 | 37 |
| | 2 | 0.04 | 0.05 | 35 | 41 | 42 |
| | 5 | 0.04 | 0.06 | 26 | 32 | 46 |
| | 5 | 0.05 | 0.05 | 32 | 39 | 39 |
| | 10 | 0.05 | 0.05 | 33 | 40 | 40 |
| | 10 | 0.03 | 0.05 | 33 | 37 | 40 |
| | 10 | 0.02 | 0.04 | 34 | 38 | 40 |

TABLE III (*continued*).

| Temp. | Acidity. vol. % $H_2SO_4$. | Color blank. | Iodine blank. | Value of permanganate. Uncorr. | Color corr. | Iodine corr. |
|---|---|---|---|---|---|---|
| 75° | 2 | 0.03 | 0.02 | 0.005141 | 0.005144 | 0.005143 |
| | 2 | 0.03 | 0.03 | 37 | 41 | 41 |
| | 5 | 0.04 | 0.025 | 37 | 42 | 40 |
| | 5 | 0.03 | 0.03 | 39 | 43 | 43 |
| | 10 | 0.05 | 0.06 | 29 | 36 | 37 |
| | 10 | 0.06 | 0.04 | 34 | 43 | 40 |
| 80 | 2 | 0.05 | 0.045 | 0.005138 | 0.005145 | 0.005144 |
| | 2 | 0.02 | 0.03 | 36 | 39 | 40 |
| | 2 | 0.04 | 0.05 | 36 | 42 | 43 |
| | 5 | 0.03 | 0.05 | 38 | 42 | 44 |
| | 5 | 0.04 | 0.04 | 39 | 44 | 44 |
| | 10 | 0.03 | 0.03 | 34 | 38 | 38 |
| | 10 | 0.03 | 0.03 | 36 | 40 | 40 |
| 86 | 2 | 0.04 | 0.03 | 0.005142 | 0.005146 | 0.005144 |
| | 2 | 0.02 | 0.03 | 40 | 43 | 43 |
| | 5 | 0.03 | 0.035 | 38 | 42 | 43 |
| | 5 | 0.02 | 0.02 | 37 | 40 | 40 |
| | 10 | 0.02 | 0.02 | 38 | 41 | 41 |
| | 10 | 0.03 | 0.045 | 35 | 39 | 41 |
| 92 | 2 | 0.02 | 0.03 | 0.005143 | 0.005146 | 0.005148 |
| | 2 | 0.02 | 0.03 | 46 | 48 | 49 |
| | 5 | 0.035 | 0.04 | 39 | 43 | 44 |
| | 5 | 0.05 | 0.05 | 32 | 39 | 39 |
| | 5 | 0.05 | 0.06 | 30 | 37 | 39 |
| | 5 | 0.06 | 0.06 | 31 | 39 | 39 |
| | 10 | 0.05 | 0.05 | 32 | 38 | 38 |
| | 10 | 0.06 | 0.06 | 30 | 38 | 38 |

TABLE IV.—EFFECT OF ACIDITY AND TEMPERATURE.

(*a*) Series 1, rearrangement of data of Table III.

| Temperature. | Acidity. vol. % $H_2SO_4$. 2%. | 5%. | 10%. |
|---|---|---|---|
| 30° | 0.005138 | 0.005133 | 0.005132 |
| 45 | 39 | 35 | 38 |
| 60 | 38 | 42 | 40 |
| 75 | 42 | 42 | 38 |
| 80 | 42 | 44 | 39 |
| 86 | 44 | 42 | 41 |
| 92 | 48 | 40 | 38 |

(*b*) Series 2.

| Temperature. | 2%. | 5%. | 10%. |
|---|---|---|---|
| 30 | 0.005646 | 0.005646 | 0.005649 |
| 60 | 50 | 48 | 48 |
| 80 | .. | 50 | .. |
| 85 | 51 | 50 | 44 |
| 92 | .. | 50 | .. |
| 95 | 53 | 52 | 46 |

Each value reported is the average of at least two determinations.

In addition to the data of Tables III and IV, those in other tables will show the same influence of temperature and acidity as are here indicated. Taking these data all together, it is certain that, though small, these influences are appreciable.

The time in the titration at which the temperature has an influence upon the result is evident from the tests of Table V. These data show that, except in its influence upon the size of the end-point correction, the temperature of the solution after the first few cc. of the permanganate have been decolorized is without appreciable effect. The significance will be apparent when considered in connection with the results of the tests given in Table VIII.

TABLE V.—TIME AT WHICH TEMPERATURE HAS EFFECT.

All titrations started in 250 cc. of 5% by volume sulfuric acid.

| Temperature: *a.* initial; *b.* during main part of titration; *c.* at end-point. | | | | | Value of permanganate. | | |
|---|---|---|---|---|---|---|---|
| *a.* | *b.* | *c.* | Color blank. | Iodine blank. | Uncorr. | Color corr. | Iodine corr. |
| 90° | 90° | 90° | 0.05 | 0.06 | 0.005130 | 0.005137 | 0.005139 |
| | | | 0.06 | 0.06 | 31 | 39 | 39 |
| 90 | 90 | 30 | 0.03 | 0.07 | 29 | 33 | 38 |
| | | | 0.03 | 0.065 | 30 | 34 | 39 |
| 90 | 30 | 30 | 0.03 | 0.09 | 25 | 29 | 37 |
| | | | 0.04 | 0.12 | 19 | 24 | 35 |
| 30 | 30 | 30 | 0.03 | 0.05 | 0.005126 | 0.005130 | 0.005133 |
| | | | 0.05 | 0.08 | 24 | 32 | 36 |
| | | | 0.04 | 0.085 | 22 | 27 | 32 |
| 30 | 30 | 90 | 0.05 | 0.06 | 25 | 31 | 33 |
| | | | 0.07 | 0.09 | 25 | 34 | 36 |
| | | | 0.05 | 0.05 | 25 | 30 | 30 |
| | | | 0.04 | 0.05 | 29 | 34 | 34 |
| 30 | 90 | 90 | 0.03 | 0.03 | 29 | 34 | 34 |
| | | | 0.03 | 0.03 | 31 | 35 | 35 |

*e. Air Access—Oxidizing Effect.*—It has been suggested[1] that during the course of the reaction atmospheric oxygen, through the carrying action of the manganous salt, might cause the oxidation of appreciable amounts of oxalic acid. To test this point, a preliminary series of experiments was made as to the results obtained on the removal of the larger part of the air from the titration vessel. To accomplish this, the solution to be titrated was made up in a flask with recently boiled water and a small amount of sodium carbonate added just before starting the titration. The carbon dioxide evolved carried out the bulk of the air, and the flask was kept stoppered and the permanganate run in through a small funnel, which passed through the stopper. From the results it

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[1] Who first suggested this is not known; Schröder has tested this point recently (*Z. öffent. Chem.*, **16**, 270 (1910)). See p. 409 for discussion of his data.

appeared that no oxidizing action of the air was to be feared; but to further test this point the following method was employed.

The solution to be titrated was placed in a glass-stoppered flask of special form (see Fig. 1) and a strong current of air or carbon dioxide, as desired, was bubbled through the liquid before commencing the titration and during its progress. When carbon dioxide was used, the solution was heated to boiling and then cooled to the desired temperature in a stream of the gas, thus ensuring the absence of all but the last traces of air.

The two series of tests made in this manner are summarized in Tables VI and VII:

TABLE VI.—EFFECT OF ACCESS OF AIR ON TITRATION.

All titrations started in 250 cc. of 5% by volume $H_2SO_4$.

| Temp. | Titration in flask with air bubbled through solution. | Titration in flask with carbon dioxide[1] bubbled through solution. | Titration in beaker open to air, as in ordinary procedure. |
|---|---|---|---|
| 30° | 0.005041 | 0.005037 | 0.005040 |
| | 40 | 38 | 39 |
| 60 | 42 | 40 | 41 |
| | 42 | 43 | 40 |
| 90 | 42 | 47 | 41 |
| | 41 | 51 | 44 |

TABLE VII.—EFFECT OF ACCESS OF AIR ON TITRATION.

All titrations started in 250 cc. of 2% by volume $H_2SO_4$.

| Temp. | Titration in flask with air bubbled through solution. | Titration in flask with carbon dioxide bubbled through solution. | Titration in beaker open to air, as in ordinary procedure. |
|---|---|---|---|
| 30° | 0.005591 | 0.005592 | 0.005591 |
| | 91 | 93 | 92 |
| 60. | 94 | 99 | 97 |
| | 94 | 99 | 97 |
| 90 | 94 | 5600 | 98 |
| | 95 | 01 | 5602 |

The data of Tables VI and VII show that no large error comes from atmospheric oxidation of the oxalate during titration. The largest difference between results obtained using air and using carbon dioxide are only one part in 500 (0.2%) and the differences were usually less than one-half this amount. Moreover, if carried out in a beaker as ordinarily done, the values obtained are not appreciably different from those where air is wholly excluded (cf. last two columns of Table VII); and even when air is bubbled through the solution during a titration at 90°, the oxidation is scarcely appreciable. No such chance for atmospheric action is

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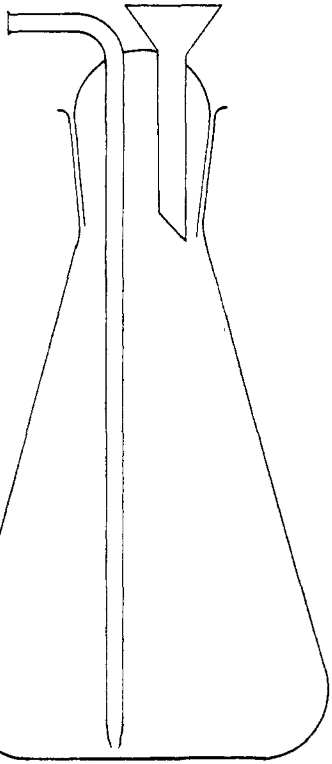
[1] The carbon dioxide used in the experiments of Table VI was found to contain 3% of methane, so the results of the tests reported in this table are only approximate. See p. 396.

met with under the ordinary conditions of titration, since when following the usual procedure the carbon dioxide formed during the reaction prevents much oxygen from the air remaining in the solution during the reaction.

Figure 1



Titration Flask, capacity 500 cc.

One other point tested was the effect of time elapsing before the beginning of the titration. Four samples were made up to 250 cc. with 5% by volume sulfuric acid and heated to 90°. Two were titrated at once, the other two after standing an hour at 90°. The four results agreed within 1 in 5500, showing that even under these rather severe conditions oxalic acid is sufficiently stable and non-volatil to prevent loss during a titration from oxidation (in the absence of manganous salts, at least), from decomposition by the sulfuric acid, or from volatilization with the steam.

As a further proof that atmospheric oxidation is not an important factor in the oxalate titration, the effect of the rate of titration may be cited. In the data of Table I, the titrations covering a period up to one hour show almost no tendency to give higher values. This is contrary to what might be expected if oxidation were taking place, as the oxidation occurring would naturally be, at least roughly, proportional to the time elapsed; and such is not the case. Experiments marked * are the only exceptions met with (see Table I).

*f. Presence of Added Manganous Sulfate.*—Since the presence of added manganous sulfate would probably influence the initial rate of the reaction, its effect upon the result of the titration was tested. A series of tests (all but the last two at 30°) was carried out with the addition of manganous sulfate at different points in the course of the reaction. One cc. of the solution of manganous sulfate added was equivalent to the manganous salt formed by the reduction of 10 cc. of the permanganate solution. The results of these experiments are given in Table VIII.

It appears from these data that unless the $MnSO_4$ be added before the beginning of the titration it has little effect upon the result obtained. However, if even a small amount is added before starting the reaction at 30°, the value obtained is the same as is ordinarily obtained at 90° without the addition of manganous salt. Addition before titration at 90° has no influence.

TABLE VIII.—EFFECT OF ADDED MANGANOUS SULFATE.

All but last two tests at 30°, last two at 90°; all started in 250 cc. of 5% by volume $H_2SO_4$.

| Amt. $MnSO_4$ solution added. | Time of addition. | Value of $KMnO_4$ found. |
|---|---|---|
| None | ........................... | 0.0 5576 |
| | | 77 |
| | | 77 |
| | | 79 |
| 1 cc. | Before start of titration | 0.005582 |
| | | 81 |
| 20 cc. | Before start of titration | 0.005583 |
| | | 83 |
| 1 cc. | After decolorization of 10 cc. of $KMnO_4$ | 0.005578 |
| | | 77 |
| 20 cc. | After decolorization of 10 cc. of $KMnO_4$ | 0.005578 |
| | | 80 |
| 1 cc. | Just before end-point | 0.005579 |
| | | 81 |
| 20 cc. | Just before end-point | 0.005578 |
| | | 78 |
| None (titrn. at 90°) | ....................... | 0.005582 |
| | | 83 |

## III. Discussion and Conclusions.

*1. Review of Possible Errors.*—As the standardization procedure consists in solution of a weighed sample in dilute sulfuric acid and direct titration with permanganate, any error occurring must be due either to error in weighing of oxalate or measuring of the permanganate or to a variation of the reaction itself from the form usually given, *viz.:*

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$

Since as already indicated (p. 397) there is no necessity for an error in either the weighing of the oxalate or the measuring of the permanganate greater than one part in 2000, only the irregularities of the reaction need be considered at length.

The variations of the reaction from its normal course may tend to cause the use of an excess of either permanganate or oxalate; or both sorts of influences may operate at the same time, in equal or unequal degree. There are nine possibilities of such irregularity; the first five of these would cause too small a consumption of permanganate, the next two an excessive use of it, and the last two might cause either of these effects. These possible sources of error are:

(*a*) Loss of oxalic acid by volatilization from the solution.
(*b*) Decomposition of oxalic acid by water.
(*c*) Decomposition of oxalic acid by sulfuric acid.
(*d*) Oxidation of oxalic acid by contact of the solution with the air.
(*e*) Presence of oxalic acid unoxidized at the end-point.
(*f*) Liberation of oxygen during the reaction.
(*g*) Presence at the end-point of unreduced permanganate or other compounds of manganese higher than manganous.
(*h*) Presence of impurities in the oxalate, either of greater or less reducing power than the oxalate.
(*i*) Formation of other products of oxidation than carbon dioxide and water.

(*a*) *Loss of Oxalic Acid by Volatilization.*—The fact that oxalic acid is readily volatile alone suggests the danger of loss from its solution by vaporization with steam. However, from the dilute solutions employed for titration purposes, no such losses occur, as has already been shown. The results obtained after an hour's standing at 90° in 5% sulfuric acid solution showed (p. 407) that no loss of oxalic acid had occurred. Similarly, when the titration extended over a period of one hour (Table I, p. 401) or when carbon dioxide or air was bubbled through the solution (Tables VI and VII, p. 406) no such higher values of the permanganate were obtained, as would have resulted had volatilization of the oxalic acid occurred. From these results it is apparent that no appreciable vaporization of oxalic acid will take place during the course of an ordinary titration, which lasts, at the most, only 5–10 minutes.

(*b*), (*c*). *Decomposition of Oxalic Acid by Water or by Sulfuric Acid.*—The same data which have shown that no volatilization occurs also prove that the water and sulfuric acid had not caused a decomposition of the oxalic acid. These possible errors can, therefore, be considered improbable under any ordinary conditions of titration.

The experiments reported by Carles,[1] from which he was led to state that at 100° oxalic acid in solution is slowly decomposed with the formation of carbon dioxide and formic acid, are not confirmed by our experiments. If such decomposition does take place, it is so slow as to have no appreciable influence upon the results of a titration made at 90° or below.

(*d*) *Oxidation of Oxalic Acid by the Air.*—Schroeder[2] has shown that in the presence of manganous sulfate, oxalic acid solutions are oxidized by the air at an appreciable speed. This author presents a large amount

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[1] *Bull. soc. chim.*, **14**, 142–4 (1870).

[2] *Z. öffent. Chem.*, **16**, 270 (1910).

of experimental data, from which he draws very decided conclusions. Those which are of importance in the present discussion are as follows (numbered as in original):

(3) "In the oxidation of oxalic acid by potassium permanganate, an error (too little $KMnO_4$ used) enters through the presence of atmospheric oxygen, which error is greater in the presence of manganous sulfate or more especially titanium dioxide.

(5) "By rapid titration in a stream of oxygen this error of No. 3 disappears, the oxygen acting on the oxalic acid to give hydrogen peroxied, which requires a corresponding amount of permanganate.

(6) "In the presence of much manganous sulfate, with oxalic acid of high concentration, especially in the presence of titanium dioxide, this hydrogen peroxide of No. 5 disappears, very rapidly if hot, and the error of No. 3 is then evident, as the compensating action of the hydrogen peroxide is not possible.

(7) "Rapid titration at 50° with 30 cc. of 1 : 1 sulfuric acid in 200 cc. of water gives results which agree with the iodine method of standardization."

Schroeder therefore recommends that the greater part of the permanganate be rapidly run into a strongly acidified solution of the oxalate and then the titration finished more slowly. Addition of manganous sulfate is not recommended.

The experimental data presented by Schroeder, which are of importance to this discussion, are those in his tables numbered 3, 4, 5, 6, 10 and 11. These data, with very few exceptions, seem to warrant the following conclusions (not expressed by Schroeder but drawn from his data):

(*a*) High temperature tends to cause a smaller permanganate consumption (Tables 3, 4, 5 and 6).

(*b*) High acidity tends to cause a high permanganate consumption (Tables 3, 4, 5, 10 and 11).

(*c*) Slow titration (10 min.) requires less permanganate than fast (1–1½ min.) titration.

(*d*) Presence of added manganous sulfate (1–5 g.) tends to cause less permanganate to be used, even with rapid titration (Tables 5 and 6).

(*e*) Titration in an air current required slightly more permanganate than in a current of carbon dioxide, when made either rapidly or slowly or in the presence of large or small amounts of acid.

It must be noted that in his experiments the stirring was very inefficient, since Schroeder often refers to his titration as "frequently whirled" (umgeschwenkt) and "whirled from time to time;" and no end-point corrections were made even when the titrations were conducted rapidly, at low temperature, or in the presence of large amounts of acid and manganous salt.

These conclusions as to the influence of conditions are confirmed, in general, by the data obtained in our own work; but it does not seem that the conclusions expressed by Schroeder (quoted p. 410) necessarily follow from the data which he presents. In fact, from his own experimental results, we would infer, as stated by us in our conclusion (*e*) (2nd preceding paragraph), that the error due to atmospheric oxidation claimed by him (see (3) p. 410) does not exist. Although it is admitted that on long standing at high temperature oxalic acid in solution in the presence of much manganous sulfate is oxidized by the air, such a combination of conditions is not met in the standardization of permanganate; and such oxidation does not take place to any such extent as claimed by Schroeder under the conditions which are properly employed. On the above basis we believe that Schroeder's conclusion (3) is not warranted, even by his own data.

If, as seems necessary, the explanation that loss of oxygen and not atmospheric oxidation is responsible for the variation of the permanganate values obtained under different conditions of titration, then the conclusions (5) and (6) expressed by Schroeder are not necessary for the explanation of the experimental data.

The fact that the use of the conditions chosen by Schroeder gave values which agreed well with those obtained by the iodine method of permanganate standardization (see (7) p. 410) would not prove that these conditions are correct, since no evidence is presented to show that the iodine standardization was carried out under conditions giving correct values. As a matter of fact, the iodine standardization is even more largely affected by conditions than is the oxalate method and none of these influences has been systematically studied.

As has already been stated (p. 406) the experimental data obtained by the author do not indicate that any appreciable atmospheric oxidation of oxalic acid occurs during the course of a standardization. Moreover, Schroeder's data warrant the conclusion that when titrations are made in a stream of air, no less (and perhaps even more) permanganate is required than if made in a stream of carbon dioxide.

Therefore, it appears certain that the oxidizing effect of the air during the permanganate-oxalate reaction will not have an appreciable influence upon the result obtained from such standardization.

(*e*) *Presence of Oxalic Acid Unoxidized at the End-point.*—In so far as our present knowledge goes, there is no evidence to indicate any incompleteness in the oxidation of the oxalic acid. Since one of the products of the reaction, the carbon dioxide, is almost wholly removed from the sphere of action, there is little if any tendency to come to an equilibrium before the whole of the oxalate is oxidized. The reaction

$$Mn^{\cdot\cdot\cdot} \text{ (or } MnO_4^-) + H_2C_2O_4 = Mn^{\cdot\cdot} + H_2O + CO_2$$

cannot be reversible under the conditions of titration; and unless it be reversible, unoxidized oxalic acid would hardly remain in the presence of an excess of permanganate. Moreover, if no free oxalic acid remains, the complex $Mn(OH)_3.xH_2C_2O_4$ could not be stable since it would be completely decomposed according to the reaction

$$Mn(OH)_3 \cdot xH_2C_2O_4 \rightleftarrows Mn(OH)_3 + xH_2C_2O_4.$$

Since the $H_2C_2O_4$ formed by this last reaction is destroyed by the $KMnO_4$ excess as fast as formed, the reaction would continue to the complete decomposition of the complex. The fact that the solution at the end of a titration contains an excess of permanganate and does not lose its oxidizing power, even after standing for half an hour or more at 90°, indicates that the oxidation of the oxalate must have been complete during the titration.

(*f*) *Liberation of Oxygen.*—In a recent article Sarkar and Dutta[1] claim that unlimited amounts of permanganate can be reduced by small amounts of organic material at high temperatures (85–90°) and high acidity by the following cycle of reactions:

(*a*) $5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = 10CO_2 + K_2SO_4 + 2MnSO_4 + 8H_2O.$

(*b*) $3MnSO_4 + 2KMnO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4.$

(*c*) $2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2.$

(*d*) $2MnSO_4 + 2KMnO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4.$

Similarly other authors have claimed that oxygen is evolved from the interaction of sulfuric and permanganic acids.[2]

In reply to Sarkar's and Dutta's claim, Skrabal[3] has proposed the following scheme as explaining the evolution of oxygen when permanganate and oxalic acid react. (Compare with this author's scheme for the normal reaction, given on p. 396.)

I. Incubation period:

$$Mn^{VII} \longrightarrow Mn^{II} + O_2 \qquad (1)$$

II. Induction period:

$$Mn^{VII} + Mn^{II} \longrightarrow Mn^{III} \begin{cases} \longrightarrow Mn^{II} + Mn^{IV} & (2) \\ \text{or} & \\ \longrightarrow Mn^{II} + O_2 & (3) \end{cases}$$

III. End period:

$$Mn^{IV} \longrightarrow Mn^{II} + O_2 \qquad (4)$$

Whether one wished to accept this last scheme, or that of Sarkar and Dutta, or even some entirely different explanation, the fact remains that oxygen may be evolved during the course of these reactions when they take place under certain conditions. Such oxygen loss would be ex-

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[1] *Z. anorg. Chem.*, **67**, 225–33 (1910).

[2] Hirtz and Meyer, *Ber.*, **29**, 2828–30 (1896). Gooch and Danner, *Am. J. Sci.*, [3] **44**, 301–10 (1892). Jones, *J. Chem. Soc.*, **33**, 95 (1878).

[3] *Z. anorg. Chem.*, **68**, 48–51 (1910).

pected under either of the following conditions, *viz.*, an increased concentration of acid or an increased concentration of $HMnO_4$ or $MnO_2$ (and possibly also of $Mn_2O_3$) in the solution. The first of these conditions is produced by direct increase in amount of acid added and the result has been shown to be an increased permanganate consumption (see Tables III and IV). The presence of $HMnO_4$, $MnO_2$ and perhaps $Mn_2O_3$, one or all, is caused by any one of the following influences:

Low temperature, which decreases the rate of their reduction to the manganous condition.

Large bulk of solution, which reduces the oxalate concentration and therefore the rate of their reduction to manganous condition; and

Rapid addition of permanganate (especially at the start or just before the end-point) or insufficient stirring, both of which allow the unreduced or partially reduced manganese to accumulate throughout or in parts of the solution.

Each of these conditions has been shown to cause an increase in the permanganate used for the titration. On the other hand, addition of manganous sulfate, which increases the rapidity of the reduction of the manganese, causes a decreased consumption of permanganate (see Table VIII).

To briefly summarize these points: the loss of small amounts of oxygen, which certainly does occur under some conditions, would account for the effect noted in all of the experiments described where change of temperature, of acidity, of volume, of rate of addition of the permanganate, of rate of stirring or the addition of manganous sulfate has an appreciable influence upon the result of the standardization. Since with proper precautions these variations can be reduced, indeed almost eliminated, over considerable range of temperature, acidity and volume of solution, there is good reason to believe that the loss of oxygen is almost, if not wholly, prevented. In this connection, it must again be emphasized that vigorous stirring throughout the titration, and slow addition of the permanganate at the beginning and at the end, are essential if correct results are to be had.

(*g*) *Incomplete Reduction of the Permanganate.*—It has been shown in the discussion of the end-point corrections (p. 399) that in addition to permanganate there is often manganic ($Mn^{\cdot\cdot\cdot}$) or tetravalent manganese ($Mn^{\cdot\cdot\cdot\cdot}$) salt present at the end-point. However, the error caused by their presence is corrected by the end-point "blank" described above and, therefore, need not be considered as influencing the results already given. In the ordinary titration, such error would be serious only if improper conditions of titration were chosen. The conditions recommended below entirely eliminate this source of error.

(*h*) *Impurities in the Oxalate.*—The question of purity of the sodium oxalate, water and acid used in the titration, must, of course, be considered; but there is no need for appreciable error to arise due to this source if the simple tests referred to above under "reagents used" are applied. As especially affecting the present discussion, this source of error has been eliminated even beyond the accuracy of the tests for purity of the oxalate, since only comparative values were employed.

(*i*) *Abnormal Oxidation Products.*—Several abnormal products of the oxidation can be imagined, for example, carbon monoxide, hydrogen, hydrogen peroxide and oxides of carbon higher than carbon dioxide. It is not at all probable that either hydrogen or carbon monoxide would result from such a reaction as that under consideration, since the former would be liberated in a nascent state very easily oxidized and the latter could be formed only by a decomposition of the oxalate molecule in a way never observed except under the action of a strong dehydrating agent, *e. g.*, concentrated sulfuric acid.

The possibility of the formation of hydrogen peroxide or higher carbon oxides has been discussed by Schroeder.[1] This could lead to error under only the first of the following two conditions, *viz.*, that they subsequently decomposed, setting free oxygen or that they remained intact at the end point. The former condition has already been discussed (p. 412); the latter possibility, that they remain unacted upon to the end of the titration, is both improbable and immaterial, since, when the end-point correction is employed, the excess of oxygen which they might contain would undoubtedly be corrected for by the "blank" as determined with potassium iodide.

## 2. Summary and Conclusions.

As is indicated in the discussion immediately preceding, there appear to be only two sources of variation from the normal course of the reaction which are at all probable, *viz.*, loss of oxygen from the solution or oxidation of part of the oxalic acid by atmospheric action. Although either of these theories explains a large part of the experimental facts, only the former can be held in the light of the experiments of Tables VII and the other facts discussed in connection with this table.

Therefore, if the main source of error is due to oxygen losses, the higher values obtained in the various series are more nearly correct. This conclusion has been accepted as a working basis for the recommendations regarding choice of conditions for titration. Indeed such choice cannot be far in error, since the greatest discrepancies noted under wide ranges of conditions is not over 0.2% (not including errors due to long standing, inefficient stirring and excessively rapid permanganate addition just at the end-point).

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[1] *Z. öffent. Chem.*, **16**, 270 (1910).

### 3. Method of Procedure Recommended.

Although it can be seen that under quite varied conditions of standardization, the values obtained for the permanganate will vary less than one part in a thousand, it seems desirable to fix more definitely the conditions of titration, both in order to make the results obtained slightly more precise and also to ensure the use of those conditions under which the difficulty of proper operation is a minimum. For this purpose the following detailed method of operation is recommended:

In a 400 cc. beaker dissolve 0.25–0.3 g. of sodium oxalate in 200 to 250 cc. of hot water (80 to 90°) and add 10 cc. of (1 : 1) sulfuric acid. Titrate at once with 0.1 $N$ $KMnO_4$ solution, *stirring the liquid vigorously and continuously*. The permanganate must not be added more rapidly than 10–15 cc. per minute and the last ½–1 cc. must be added dropwise with particular care to allow each drop to be fully decolorized before the next is introduced. The excess of permanganate used to cause an end-point color must be estimated by matching the color in another beaker containing the same bulk of acid and hot water. The solution should not be below 60° by the time the end-point is reached; more rapid cooling may be prevented by allowing the beaker to stand on a small asbestos covered hot plate during the titration. The use of a small thermometer as stirring rod is most convenient in these titrations, as the variation of temperature is then easily observed.

### 4. Accuracy and Precision Attainable.

The agreement of duplicates in the numerous tables given above shows the precision which can be expected in the use of sodium oxalate when the conditions of titration are regulated. It appears that agreement of duplicates to one part in two thousand should be regularly obtained if weight burets are used. Failure to obtain this precision should be at once taken to mean that some condition has not been regulated with sufficient care.

Although the absolute accuracy of the values obtained under different conditions has not yet been studied, it seems probable that if the method recommended is followed the error will not exceed 0.1% and probably will be less than 0.05%.

It is hoped to undertake a comparison of this method with other oxidimetric standards, particularly iron, silver, and iodine, in order to check its value. However, such work involves one uncertainty which renders the best results which could be obtained probably no more conclusive than those now at hand. The difficulty is that of end-points, for in each case mentioned the uncertainty in the blank correction required for an end-point is about of the same order as that of the uncertainty in the oxalate values, namely, 0.1% (usually equivalent to 0.05 cc. of 0.1 $N$

$KMnO_4$). We, therefore, at the present time, would assume no greater absolute accuracy for the values obtainable than 0.1%.

The author takes pleasure in acknowledging the kindness of Dr. W. F. Hillebrand in giving valuable advice during the course of the work reported in this article.

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# THE CARD INDEX TO CHEMICAL LITERATURE OF THE UNITED STATES PATENT OFFICE.

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Received January 9, 1912.

Previous papers, fully describing the system used, have been published in THIS JOURNAL, **22**, 478 (1900) and **29**, 936 (1907), this paper being in the nature of a report of progress, the index now containing about 1,200,000 cards, of which 700,000 are chemical titles and names of substances and 500,000 are formula cards. At the present time a force of four persons is at work in keeping up to date with the bimonthly issues of the Abstracts of the Society, which receive a very minute treatment, some of the half and quarter page abstracts in the Organic section at times giving rise to from 50 to 200 cards each, as every substance named is carded. Our force, however, is not sufficient to do all that has been blocked out as desirable, and some work which we hope to do in the future is now in abeyance for lack of force, *e. g.:*

*J. Chem. Soc. (London)*, from 1907 to date.

Supplements to Richter's "Lexikon der Kohlenstoff Verbindungen."

Remaining volumes of "Beilstein."

Wurtz's "Dictionnaire de Chimie."

Watts' "Dictionary of Chemistry" (4-vol. edition).

And some other works which I will not take time to mention, to say nothing of the large number of chemical patents not yet indexed.

For convenience of reference I append a table showing the work done since 1907 (for previous work see the articles already published), so that any one caring to make use of the index can know exactly what is the field covered, which, including the English abstracts to 1907 and our own to date with the exception of Vols. 1 and 2, which will eventually be included, is fairly complete.

This index, while intended primarily for the use of the office in the granting of chemical patents, is thrown open to the general public without charge, any one beinga llowed to consult it and make extracts from it without payment of fees, and more than once advanced students of our universities have greatly lightened their labors in the examination of literature in preparing their theses, and its use by patent solicitors and attorneys and chemical engineers in investigating questions of patenta-