out that the properties of these groups in the free state correspond to those of elements of the same electro-affinity. Groups intermediate in the series exhibit marked amphoteric properties; that is, they appear in an electronegative or electropositive state, depending on conditions.

The properties of the univalent amphoteric groups correspond closely to those of hydrogen, which is the only univalent amphoteric element known. The properties of the trimethylstannyl group and its compounds are discussed in detail and compared with those of hydrogen.

WORCESTER, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE STANDARDIZATION OF THIOSULFATE SOLUTION BY THE PERMANGANATE-IODIDE AND DICHROMATE-IODIDE METHODS

BY WILLIAM C. BRAY AND HARRY EAST MILLER

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Vosburgh's recent investigation[1] has probably settled two important problems in volumetric analysis. (1) Potassium dichromate as a standard in iodimetry is accurate within 0.1%, provided the concentrations of acid and iodide are maintained within rather narrow limits during the reaction between dichromate and iodide. The chief sources of error are the slowness of this reaction when the concentrations of acid and iodide are too low, and the liberation of iodine by oxygen when these concentrations are too high. (2) The iodine-thiosulfate titration should always be made in dilute acid, rather than neutral, solution. An explanation of the small error of 0.1 to 0.3% in neutral solution was not given by Vosburgh but is almost certainly the formation of a minute amount of sulfate instead of tetrathionate. That thiosulfate is oxidized completely to sulfate by iodine in alkaline solution, which would correspond to an error of 800% if the product were assumed to be tetrathionate, has been discovered independently by several investigators.[2] If, as seems probable, hypo-iodite and hypo-iodous acid are responsible for this reaction, then the presence of acid eliminates the error by repressing the hydrolysis of iodine.[3]

A third result, given by Vosburgh in the last paragraph of his paper, seemed questionable. He concluded that a permanganate solution, the concentration of which is determined with sodium oxalate by McBride's method,[4] is unreliable as a standard in iodimetry. The error

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[1] Vosburgh, THIS JOURNAL, **44**, 2120 (1922).

[2] Abel, *Z. anorg. Chem.*, **74**, 393 (1912). References to earlier work are given. Compare Bray, Simpson and MacKenzie, THIS JOURNAL, **41**, 1376 (1919), for similar results in Na_2HPO_4 solution.

[3] Bray, THIS JOURNAL, **32**, 932 (1910). Bray and Connolly, *ibid.*, **33**, 1485 (1911).

[4] McBride, *ibid.*, **34**, 415 (1912). See Ref. 11.

with reference to the dichromate method was 0.4%, and was in the direction corresponding to the liberation of too little iodine in the permanganate-iodide reaction. We had for several years used this permanganate method[5] of standardizing thiosulfate solution, and had found it to be reproducible to 0.1%. Evidence of its accuracy is furnished by the results of Milobendzki,[6] who claimed to have worked within 0.03%. He found an error of only 0.1%, in the direction that too much iodine is liberated in the permanganate-iodide reaction. Bray and MacKay[7] found the error in this direction to be not more than 0.15 to 0.2%, which was probably not much beyond the limit of accuracy of their work. In both these investigations the thiosulfate solutions were standardized against pure iodine, and it is possible that the iodine-thiosulfate titrations were made in neutral, and not in faintly acid solutions. If so, a small correction should be applied, which would lessen or even change the sign of the observed error. In any event, there was a discrepancy of 0.3 to 0.6% between these results and that of Vosburgh, and the question required further investigation. We have found that the permanganate and dichromate methods agree within 0.1%.

The conclusion that the permanganate method is accurate to 0.1% has also been reached in two other recent investigations, by Popoff and Chambers,[8] and by Hendel.[9] The value of the evidence of Popoff and Chambers is greatly lessened by the fact that the iodine-thiosulfate titrations were made at such high concentrations of acid and iodide that in the 15 minutes required for their electrometric titration an appreciable amount of iodine would have been liberated by the reaction between oxygen, iodide and acid. In blank experiments made by us, without the addition of iodine or permanganate, this oxygen error corresponded to

[5] Volhard, *Ann.*, **198**, 333 (1879).

[6] Milobendzki, *Z. analyt. Chem.*, **46**, 18 (1907).

[7] Bray and MacKay, This Journal, **32**, 1198 (1910). This result has been misquoted by Laird and Simpson [*ibid.*, **41**, 527 (1919)] who state that the error was 0.2 to 0.3% in the opposite direction to that found. This misstatement was accepted by Hendrixson, *ibid.*, **43**, 1314 (1921).

[8] Popoff and Chambers, This Journal, **45**, 1358 (1923). The statement, p. 1359, that hypo-iodite does not react with thiosulfate is incorrect since, as pointed out above, sulfate is formed in any solution that contains appreciable amounts of hypo-iodite or hypo-iodous acid. On account of this formation of sulfate, the lowest concentration of hydrogen ion permissible in the arsenious acid-iodine titration, calculated by Washburn and referred to by the authors, has no significance in the thiosulfate-iodine case.

[9] Hendel, *Z. analyt. Chem.*, **63**, 321 (1924). On p. 323 there seems to be a serious misprint. It is stated that too much iodine was liberated whenever the acid concentration was "too small." This should be "too large," since the oxygen error is appreciable at higher concentrations of acid, and this error is referred to later in his article. Besides, our own experiments have shown that there is no "overoxidation" at concentrations of acid much below Hendel's lower limit, 0.1 *N*. The corresponding misstatement is made in the abstract, *C. A.*, **18**, 1447 (1924).

0.5 to 0.7 cc. of 0.01 *N* thiosulfate solution. Hendel found that the three methods of standardizing thiosulfate solution, namely the iodine, dichromate and permanganate methods, agreed within 0.1%; and that the concentrations of acid and iodide in the permanganate-iodide reaction could be varied within wide limits. During the iodine-thiosulfate titration the acid concentration was always approximately 0.1 *N*. In a set of seven permanganate experiments by his regular procedure the average deviation from the mean is stated to have been ±0.05%, and in another set of seven experiments under varying conditions this deviation is ±0.07%. The latter results, which are given in detail, show extreme variations slightly greater than ±0.1%. The results are probably as satisfactory as could be expected with volume burets, which he seems to have used.

Our work was similar in many respects to that of Vosburgh[1] and Hendel[9] and, therefore, many details need not be given. To minimize loss of iodine, we used glass-stoppered flasks and avoided vigorous agitation while the reagents were being mixed and during titration with thiosulfate solution. The following *procedures* were used when the two methods of standardization were being compared.

The *dichromate* solution (about 25 cc. of 0.1 *N*) was added from a pipet or weight buret to a solution containing 2.0 g. of potassium iodide and 20 milli-equivalents of hydrochloric acid, the final volume being 100 cc. This mixture was set aside in the dark for ten minutes, then diluted to 500–600 cc., and titrated with the stock thiosulfate solution. The acid concentration thus decreased from 0.2 to about 0.14 *N* during the reaction, and was between 0.02 and 0.03 *N* during the titration.

This procedure is similar to that recommended by Vosburgh, except that the dichromate is added last instead of the potassium iodide. The concentrations of acid and iodide correspond to the lower limit given by him.

The *permanganate* solution (about 25 cc. of 0.1 *N*) was added to 400 cc. of solution containing 2.5 g. of potassium iodide and 12.5 milli-equivalents of sulfuric acid, and after a minute the mixture was titrated with thiosulfate. The acid concentration was approximately 0.02 *N* during this titration. The permanganate-iodide reaction is so rapid that it is unnecessary to provide for higher concentrations of acid and iodide during the reaction, as with dichromate. For the same reason, solid iodine separates when potassium iodide is added last instead of the permanganate, and there is then greater danger of loss of iodine by volatilization.

In both cases starch solution was added just before the end of the titration. For accurate work it is recommended that the 0.1 *N* thiosulfate solution be added until the blue starch color has just disappeared, and that the end-point be obtained by adding a 0.01 *N* solution of iodine in potassium iodide drop by drop until a faint but distinct blue appears.

Tests of the permanganate method under widely different experimental conditions showed that it was altogether unnecessary to follow the above standard procedure, thus confirming Hendel's conclusion. Of course, when the concentrations of acid and iodide were too high, too much iodine was liberated, due to the oxygen error. Our observations on the concentrations at which this error becomes appreciable agree fairly well with those of Vosburgh and of Hendel. The following results were obtained with concentrations of acid and iodide very close to the upper limit.

The reaction was allowed to take place in 100 cc. containing 3 g. of potassium iodide, 60 milli-equivalents of sulfuric acid and the permanganate; the mixture after standing in the dark for five minutes was diluted to 400 cc. and titrated with thiosulfate. In four experiments with weight burets, in which the permanganate was added last, the weight ratios (thiosulfate/permanganate) were 1.0812, 1.0818−, 1.0810 and 1.0810, as compared with 1.0813 ± .03% by the standard procedure. In two other experiments, performed at the same time, when the potassium iodide was added last, solid iodine separated and redissolved. The ratios, 1.0802 and 1.0797, were low and show that the error due to volatilization of iodine may reach 0.1% when solid iodine is formed.

When the two sources of error referred to in the preceding paragraph were avoided, the thiosulfate-permanganate ratio obtained under widely different experimental conditions always agreed with that obtained by the standard procedure. The extreme variations did not exceed ±0.1% when volume burets were used, and ±0.05% with weight burets, and were usually smaller, especially with weight burets. No trends were observed when the following variations were made: time allowed for the reaction, 0.3–10 minutes; volume during the reaction, 75–600 cc.; potassium iodide, 1.5–10 g.; sulfuric acid, 5–60 milli-equivalents; and acid concentration during titration, 0.004–0.2 *N*.

The results at very low acid concentration are of interest. Payne,[10] who was one of the first to recommend the permanganate method, states that only enough acid is needed in the iodine reaction "to keep the manganese in solution," that is, to prevent the formation of manganese dioxide. We found that 5 milli-equivalents of acid were sufficient for this purpose when the amount required in the reaction was 3 milli-equivalents. When 2.5 milli-equivalents of acid were used, which was less than the required amount, a large precipitate of manganese dioxide formed before the addition of the permanganate solution was complete; but even then the results (with weight burets) were perfectly satisfactory provided that, before titration with thiosulfate, enough acid was added to dissolve the manganese dioxide.

In our first comparison of the permanganate and dichromate methods, with calibrated volume burets, eight determinations by each method gave the following average values for the concentration of a thiosulfate solution: 0.10127 *N* ± 0.1%, and 0.10114 *N* ± 0.08%. The discrepancy between the two methods, 0.13%, was in the direction claimed by Vosburgh, but it was within the experimental error. The extreme variation of ± 0.1% in the permanganate method was made up of ± 0.04% in the permanganate-thiosulfate, and at least ± 0.06% in the oxalate-permanganate determination.

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[10] Payne, *J. Anal. Appl. Chem.*, 6 (Sept., 1892).

We were not satisfied with these results and found it possible to increase the accuracy. Weight burets were substituted for the volume burets. The titration end-points were determined more carefully. The final use of 0.01 *N* iodine solution in the iodine-thiosulfate titration has already been mentioned. The accurate determination, after *each* permanganate-oxalate titration, of the excess of oxidizing agent present is very important. We used the iodimetric method suggested by Bray[11] instead of the color-matching method recommended by McBride.[4] The amount of sodium oxalate (from the Bureau of Standards) used in each determination, while never less than 0.3 g., seems rather small; and it is probable that the accuracy would be increased by weighing out larger amounts to give known solutions, and titrating two or more weighed portions of each solution with permanganate. (This is the method used in the dichromate standardization of thiosulfate.)

In the dichromate solutions used in the earlier work there separated on standing a small flocculent precipitate, probably of nearly negligible weight. This impurity was not destroyed by heating the dichromate near its fusion point, and remained after repeated crystallization. It was found, however, that when the dichromate was allowed to crystallize slowly, much of the impurity precipitated with the first portion. After a second similar fractionation, dichromate was obtained which yielded solutions that remained almost perfectly clear for months. Contact between filter paper and the dichromate solutions was avoided.

While the work of improving the methods was in progress, four comparisons of the two methods of standardizing thiosulfate were made at intervals, with weight burets. Two permanganate and four dichromate solutions were used. Each comparison was based on two to four measurements of the three ratios, oxalate-permanganate, permanganate-thiosulfate and dichromate-thiosulfate. The thiosulfate concentrations determined by the two methods differed by only 0.04%, 0.06%, 0.02% and 0.10%, the permanganate method yielding the higher result as before. The chief error seemed to lie in the permanganate standardization, and it was probable that the difference between the last two results was due mainly to this cause, and not to a difference in concentration of the dichromate solutions.

Accordingly a final comparison was made, using these two dichromate solutions, Nos. 8 and 9, and a new permanganate solution. The latter, after it had stood for two weeks, was carefully standardized against sodium oxalate, with the following results: with separate portions of oxa-

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[11] Bray, This Journal, **32**, 1204 (1910). Compare Ref. 4, pp. 398–400. The correction corresponded to between 0.017 and 0.05 cc. of 0.1 *N* solution. It was noted that the depth of the permanganate color at the end-point corresponded qualitatively with the magnitude of the correction.

late, 0.10689, 0.10692, 0.10687 *N;* with portions of one oxalate solution, 0.10691, 0.10685, 0.10687, 0.10690 *N*. The value 0.10690 was chosen for the weight-normality of the permanganate solution.

The results on the standardization of a thiosulfate solution by the two methods are shown in Table I.

TABLE I

STANDARDIZATION OF A THIOSULFATE SOLUTION

Permanganate method, *N*	0.09885	0.09885	0.09881	0.09885	0.09886	av. 0.09885
Dichromate method, *N*	(No. 8)0.09882	0.09879	0.09873	(No. 9)0.09877	0.09879	av. 0.09878

The two methods differ by only 0.07%, but this seems to exceed the experimental error. The difference is in the same direction as in our earlier experiments, and signifies either that too little iodine is formed in the permanganate-iodide reaction, or too much in the dichromate reaction. The similar small difference found by Vosburgh between the iodine and dichromate methods was also in the direction corresponding to the liberation of too much iodine in the dichromate-iodide reaction. We may, therefore, conclude that the three methods agree within 0.1% and that the permanganate and iodine methods probably agree more closely with each other than with the dichromate method.

A large number of experiments were performed on the effect of varying the experimental conditions in the dichromate-iodide reaction. The results with weight burets are given in Table II. They agree closely with the more numerous results previously obtained with volume burets.

TABLE II

EFFECT OF VARYING THE CONDITIONS IN THE DICHROMATE-IODIDE REACTION

Volume of solution containing acid, iodide and dichromate, 100 cc. Time allowed for the reaction, 10 min. (except in the three cases noted). Volume during titration with thiosulfate, 600 cc.

Series A. Dichromate solution added last, and rather slowly.
Series B. Potassium iodide solution added last, rapidly from a graduated cylinder.

	HCl, milli-equiv.	KI, g.	Excess of iodine referred to standard dichromate procedure
Series A	20	2	0%
	20	3	0.15, 0.17%
	60	2	0.25, 0.36%
	60	3	0.43 (5 min.); 0.40, 0.42, 0.45%
Series B	20	2	0.02, −0.04%
	60	3	(5 min.) 0.0, 0.04%

The results in Series B, where the potassium iodide solution was the last reagent added, as in Vosburgh's procedure, agree closely with those obtained in our standard procedure (line 1 of Series A), and thus confirm Vosburgh's conclusion with regard to the permissible limits for the concentrations of acid and iodide. On the other hand, when the dichromate solution was added last, as in our procedure, the results in Series A show that between 0.4% and 0.45% too much iodine is liberated when the concentrations of acid and iodide are 3 and 1.5 times those in the standard procedure. This error must be due to the presence of oxygen.

We are thus forced to the conclusion that the reaction between oxygen, iodide and acid, which is practically negligible under these conditions, is catalyzed during the dichromate-iodide reaction, when iodide is present in excess. As an explanation, it is suggested that an intermediate compound is formed by the interaction of oxygen, iodide ion and dichromate ion, and that this compound reacts with iodide in acid solution to form iodine, and with dichromate to form oxygen. A peroxide or peroxy acid would have such properties.

On account of the rapid increase of the oxygen error in Series A with increasing concentrations of acid and iodide, it seems improbable that this error is actually zero in our standard procedure or that of Vosburgh. Thus if the excess of iodine in the last column of Table II were referred to the permanganate method, then instead of the sudden rise from 0 to 0.43% in Series A, we should have a more gradual increase from 0.07 to 0.50%. This conclusion is supported by the fact that the slight discrepancy which Vosburgh found between the results obtained by the dichromate and iodine methods can also be explained by assuming a very small oxygen error in the dichromate method.

Summary

The concentration of thiosulfate solutions has been determined by means of permanganate solutions standardized against sodium oxalate, and dichromate solutions made by weighing pure potassium dichromate. The permanganate and dichromate methods are shown to agree within 0.1%. From the results of Vosburgh's careful comparison of the iodine and dichromate methods an almost exact agreement of the permanganate and iodine methods is to be expected.

The amount of iodine liberated in the reaction between permanganate, iodide and acid is constant when the volume of the solution and the quantities of iodide and acid are varied between wide limits. This is evidence against the existence of side reactions and in favor of the use of a permanganate solution in iodimetry.

In the corresponding dichromate reaction, however, the experimental conditions must be carefully controlled, especially when oxygen is present. A variation of the concentrations of acid and iodide within the rather narrow range recommended by Vosburgh is permissible but only when the iodide solution is the last reagent added, as in his procedure. When the dichromate is added last, the oxygen error is shown to increase rather rapidly with increasing concentrations of iodide and acid within the limits recommended by Vosburgh. The error is over 0.4% under conditions in which there was no error in the permanganate reaction.

It is probable that the slight discrepancy between the dichromate and the permanganate (or iodine) methods is due to an oxygen error of less than 0.1% in the dichromate-iodide reaction.

A theory is suggested for the catalysis of the reaction between oxygen, iodide and acid during the reduction of dichromate by iodide.

BERKELEY, CALIFORNIA

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THE APPLICATION OF THE PHASE RULE TO GALVANIC CELLS

BY JAMES A. BEATTIE[1]

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The deduction of the phase rule by any of the many methods that have been used requires that the separate parts of the system under consideration be in equilibrium. It is therefore necessary, before proceeding to apply the phase rule to galvanic cells, to discuss them from this standpoint.

A system is in stable equilibrium when, if any of its internal variables (such as pressure, temperature, concentration, etc.) is slightly changed, the state of the system adjusts itself so as to oppose this change; and if this disturbing influence is removed, the system will restore itself to its original state. The case of neutral equilibrium, in which an infinitesimal disturbance of an internal variable causes no alteration in the state of the system, seldom if ever occurs in chemical systems and hence will not be considered here.

In general, galvanic cells, when their potentials are exactly balanced by an opposing electromotive force, as when measured on a potentiometer, may be considered to be in equilibrium.[2] Consider the concentration cell

$$\text{Pt, } H_2(1 \text{ atm.}) \mid HCl\ (C') \mid HCl\ (C'') \mid H_2(1 \text{ atm.}), \text{ Pt} \qquad \text{(A)}$$

when its potential is so balanced. If the applied electromotive force is slightly increased (other conditions being kept constant) current will flow through the system in such a manner as to transfer HCl from the more dilute to the more concentrated solution, thus increasing the potential of the cell; and if the external electromotive force is restored to its original value, current will flow through the cell in the opposite direction until the concentrations of the solutions are again C' and C''. The other variables of the system can be treated in the same manner, and hence the system is in equilibrium.

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[1] National Research Fellow in Chemistry.

[2] Throughout this discussion the electromotive force of the cell is always considered as balanced by an equal and opposite potential. A cell that is in equilibrium under these conditions will also be in equilibrium when connected to a condenser (or, what amounts to the same thing, is on open circuit). Adding an electric charge to the plates of the condenser or subtracting one from them corresponds to increasing or decreasing the potential opposing that of the cell.