

ART. V.—*The Determination of Selenious Acid by Potassium Permanganate*; by F. A. GOOCH and C. F. CLEMONS.

[Contributions from the Kent Chemical Laboratory of Yale College—XL.]

THE fact that sulphurous and tellurous acids may be oxidized quantitatively by a sufficient excess of potassium permanganate suggests naturally the application of the same general method to the determination of selenious acid. It is the object of this paper to record the results of experiments in this direction.

Brauner* found that in the action of the permanganate upon tellurous acid, whether in a solution acidified with sulphuric acid or made alkaline by caustic soda, the reduction of the permanganate does not proceed to the lowest degree of oxidation, the tellurous acid being unable to reduce the higher hydroxides of manganese which separate. In employing the reaction quantitatively it is necessary, therefore, to add the permanganate in distinct excess and then to destroy the surplus by means

* Jour. Chem. Soc., 1891, p. 238.

of standard oxalic acid added to the solution acidified with sulphuric acid, subsequently determining the excess of oxalic acid in the warmed solution by addition of more permanganate. The difference between the amount of permanganate actually used and that required to oxidize the known amount of oxalic acid introduced should naturally be the measure of the tellurous acid acted upon. Brauner found, however, an error in the process, by no means inconsiderable, due to the decomposition of the permanganate outside the main reaction. In a subsequent paper from this laboratory* it was shown that if the precaution is taken to restrict the amount of sulphuric acid present in the solution when the permanganate acts the secondary decomposition involving loss of unutilized oxygen is kept within narrow bounds. In our work upon the oxidation of selenious acid we have followed the suggestions gained in the treatment of tellurous acid by Brauner's method.

The selenium dioxide which we employed was prepared from so-called pure selenium by dissolving the element in strong nitric acid, removing the nitric acid by evaporation, treating the aqueous solution with barium hydroxide to throw out any selenic acid formed in the oxidation, evaporating the solution to dryness, and subliming and re-subliming the residue in a current of dry air until the product was white. The oxide thus prepared was weighed out for individual experiments or was dissolved in a standard solution from which definite portions were drawn for use.

In the first series of experiments, the results of which are recorded in Table I, the selenium dioxide was dissolved in 100 cm³ of water, 10 cm³ of sulphuric acid of half-strength were added, an approximately decinormal standardized solution of potassium permanganate was added until the characteristic color predominated over that of the brown hydroxide deposited during the oxidation, oxalic acid in solution of known strength was introduced until the excess of permanganate had been destroyed and the insoluble hydroxide dissolved, and, finally, after heating the solution to about 80° C., more of the permanganate was added to the color reaction. The final volume varied from 250 cm³ to 350 cm³, so that the sulphuric acid (absolute) present varied from about five per cent at the start to from one and a half to two per cent at the end.

When the permanganate is first introduced into the acidified solution the color vanishes, leaving a clear colorless liquid, but as more is added the solution becomes yellow and deepens gradually in color to a reddish brown, until turbidity due to the deposition of a brown hydroxide of manganese ensues, and finally the characteristic color of the permanganate is plainly

* Gooch and Danner, this Journal, xlv, 301.

distinguishable. The exact point at which precipitation of the manganic hydroxide begins depends upon the dilution, acidity, and temperature of the solution. In experiments (1) and (2), the permanganate was added to the cold solution at the first, but the liquid was heated after the addition of oxalic acid and before the final titration with the permanganate. The remaining determinations of the series were made in solutions kept hot throughout.

TABLE I.
[Se=79.1, O=16.]

	SeO ₂ taken. gram.	Oxygen equivalent of permanganate used. gram.	Oxygen equivalent of oxalic acid used. gram.	SeO ₂ found. gram.	Error. gram.
(1)	0.1000	0.03026	0.01571	0.1010	0.0010 +
(2)	0.1002	0.03038	0.01578	0.1014	0.0012 +
(3)	0.0997	0.02634	0.01182	0.1008	0.0011 +
(4)	0.0999	0.02568	0.01122	0.1004	0.0005 +
(5)	0.1000	0.02536	0.01077	0.1012	0.0012 +
(6)	0.1000	0.03226	0.01765	0.1015	0.0015 +
(7)	0.1001	0.04455	0.02992	1.1016	0.0015 +
(8)	0.2001	0.05448	0.02543	0.2018	0.0017 +
(9)	0.1997	0.05219	0.02318	0.2014	0.0017 +
(10)	0.1997	0.05215	0.02318	0.2011	0.0014 +
(11)	0.5178	0.13215	0.05721	0.5203	0.0025 +
(12)	0.5197	0.14105	0.06541	0.5252	0.0055 +

An examination of these results develops the fact that the action proceeds regularly in the main under the conditions of experimentation, but that there is an apparent waste of permanganate in the process. It was observed that the addition of a little permanganate beyond the exact amount necessary to produce the end-reaction occasioned the precipitation of manganese hydroxide, evidently, according to Guyard's reaction, by interaction between the permanganate and the manganous sulphate present. Plainly the amount of sulphuric acid present, which we kept purposely low to obviate the spontaneous decomposition of the permanganate, was not sufficient to prevent the ultimate formation of the hydroxide at the temperature of action. The natural inference is that the difficulty in the determinations may have been due rather to an interference with the color reaction at the end of the oxidation process, due to the incipient tendency of the permanganate to act upon the manganous salt, than to direct loss of oxygen from the permanganate. If this is true, the obvious and simple remedy should be found in effecting the oxidation of the oxalic acid at the end of the process at a temperature so low that the inclination of the permanganate and manganous sulphate to interact shall be diminished. Table II contains the record of experi-

ments in which this precaution was taken. The entire process of oxidation, which was otherwise similar to that of the previous experiments, was brought about between the temperature of 75° C. at the beginning and 50° C., or even a little less, at the end. The end-reaction was in every case sharp and the final color was permanent for several minutes at the least.

TABLE II.

	SeO ₂ taken, grm.	Oxygen equivalent to permanganate used, grm.	Oxygen equivalent to oxalic acid used, grm.	SeO ₂ found, grm.	Error. grm.
(13)	0.1000	0.03506	0.02065	0.1001	0.0001 +
(14)	0.1000	0.03519	0.02073	0.1004	0.0004 +
(15)	0.1000	0.03706	0.02255	0.1007	0.0007 +
(16)	0.1000	0.03853	0.02422	0.0994	0.0006 —
(17)	0.1000	0.03512	0.02065	0.1005	0.0005 +
(18)	0.2000	0.06124	0.03256	0.1994	0.0006 —
(19)	0.2011	0.06069	0.03177	0.2008	0.0003 —
(20)	0.2004	0.06072	0.03177	0.2010	0.0006 +
(21)	0.2020	0.06083	0.03185	0.2012	0.0008 —
(22)	0.2038	0.06106	0.03185	0.2028	0.0010 —

These results are evidently an improvement upon those of the first series of experiments, and are fairly satisfactory so far as concerns the estimation of the amounts of selenium dioxide discussed. The determination of large amounts of selenious acid by this method is somewhat less advantageous than it would be if the reduction of the permanganate proceeded farther in the first action. One hundred cubic centimeters of a standard solution is as much as can be conveniently handled in a single process of titration, and that volume of decinormal permanganate (which is about as strong as the standard solution should be when accurate work is expected) is capable of oxidizing about 0.25^{grm} of selenium dioxide.

The process which we recommend consists, in brief, in the addition of standard potassium permanganate to the solution of selenious acid containing not more than five per cent of its volume of strong sulphuric acid, the introduction of standard oxalic acid until the liquid clears, and the titration of the excess of oxalic acid by permanganate, at a temperature not much exceeding 50° or 60° C. The permanganate and the oxalic acid should be standardized under similar conditions of acidity and temperature, and for a standard of final reference we prefer pure crystallized ammonium oxalate.

We have made experiments in which the initial oxidation of the selenious acid was made in alkaline solution, but inasmuch as the amount of permanganate required for the oxidation is about three times as great as that needed in the acid solution the treatment in alkaline solution is practically inferior.