ART. VII.—*The Iodometric Determination of Selenious and Selenic Acids;* by F. A. GOOCH and A. W. PEIRCE.

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

IT has been shown in a recent paper from this laboratory* that the simple contact of solutions of selenious acid, potassium iodide, and hydrochloric acid according to the recommendation of Muthman and Schaefer† is not enough to effect the liberation of the theoretical amount of iodine when the assumption is made that the selenium of the selenious acid is all reduced to the elementary condition. On the other hand, it was found that the yield of iodine is complete when such mixtures are submitted to distillation under well-defined conditions. It is necessary, however, to estimate not only the iodine which passes to the distillate, but that which is retained in small proportion in the residue, and, though this method of proceeding yields closely accurate analytical results and is by no means difficult, it is obvious that a process so contrived that the reduction of the selenious acid should be registered entirely in the residue would possess the advantage in point of convenience. We have made the attempt, therefore, to apply in this case a principle of action laid down in a method elaborated in this laboratory for the estimation of chlorates.‡ When a solution of arsenic acid containing potassium iodide and sulphuric acid is boiled under defined conditions§ the arsenic acid is reduced to arsenious acid with liberation of iodine. When the arsenic acid is in excess the whole of the iodine is evolved and the arsenious acid produced is its exact measure. Upon making the solution alkaline with acid potassium carbonate, the arsenious acid may be re-oxidized by standard iodine, and the amount of iodine thus used will be the exact equivalent of that set free in the reduction-process. If, however, any other substance more easily reducible than arsenic acid is present, such substance should, naturally, take its part in liberating iodine from the iodide and the reduction of the arsenic acid should be correspondingly less. This was found to be the case when a mixture containing a chlorate, arsenic acid, potassium iodide, and sulphuric acid was boiled under regulated conditions, so that, with a knowledge of the amount of iodide employed and the determination of the quantity of

* Gooch and Reynolds, this Journal, l, 254.
† Ber. d. Chem. Gesell., xxvi, 1008.
‡ Gooch and Smith, this Journal, xlii, 220.
§ Gooch and Browning, this Journal, xxxix, 188.

iodine necessary to reoxidize the arsenious acid produced, the data were at hand for calculating the amount of chlorate present in the mixture. It was our hope (which proved to be well-founded, as the sequel shows) that selenious acid would behave like a chlorate under similar conditions.

Pure selenium dioxide was prepared by oxidizing presumably pure selenium in strong nitric acid, evaporating the solution to dryness, dissolving the residue in water, treating the solution with barium hydroxide until precipitation ceased, filtering, evaporating the filtrate to dryness, subliming the selenium dioxide from the residue, and resubliming that product in a current of dry oxygen (which we found to be vastly more convenient and effective than dry air) until it was perfectly white and crystalline. From the oxide thus made a standard aqueous solution was prepared, from which portions were measured and (for the sake of greater accuracy) weighed for use in the experiments to be detailed. To each weighed portion of the selenious acid, contained in an Erlenmeyer flask of 300 cm^3 capacity, was added a weighed amount of potassium iodide (somewhat in excess of that theoretically required) prepared in solution of convenient strength and tested as to its reducing power upon arsenic acid under the conditions of the experiments; a solution containing about 2 grm. of pure di-hydrogen potassium arseniate was introduced; and, finally, 20 cm^3 of sulphuric acid of half-strength. Protected from ordinary mechanical loss by a trap (consisting of a two-bulbed drying tube cut short and hung loosely with the wide end downward in the mouth of the flask) and from violent ebullition by the introduction of a few bits of porcelain, the liquid was boiled until the volume decreased according to indicating marks on the flask from 100 cm^3 or more to 35 cm^3—concentration to about this lower limit having been found to be necessary to the completion of the reaction. The residue was cooled, the acid was nearly neutralized with potassium hydroxide, acid potassium carbonate was added until it was present to the amount of 20 cm^3 of its saturated solution in excess of the quantity needed to complete neutralization, and, after the addition of starch, standard iodine was introduced until the starch-blue appeared. The iodine introduced measured the arsenious acid (and so the quantity of iodine set free by the arsenic acid), and the difference between it and the iodine originally present in the form of the iodide represents the amount set free by the selenious acid.

The following table comprises the details and results of a series of determinations made in the manner outlined:

Se = 79·1, O = 16

Initial volume. cm^3.	Final volume. cm^3.	H_2SO_4 half-strength. cm^3.	Di-hydrogen-potassium arseniate. grm.	KI taken. grm.	SeO_2 taken. grm.	SeO_2 found. grm	Error. grm.
100	35	20	2	1·3277	0·1280	0·1275	0·0005—
"	"	"	"	1·0429	0·0998	0 0994	0·0004—
"	"	"	"	1·0887	0·1024	0·1028	0·0004+
"	"	"	"	1·0405	0·1036	0·1028	0·0008—
"	"	"	"	1·0721	0·1030	0·1029	0 0001—
"	"	"	"	0·9958	0·1273	0·1272	0 0001—
125	"	"	"	2·0828	0·1997	0·2000	0·0003+
"	"	"	"	2·2272	0·2110	0·2113	0·0003+
"	"	"	"	2·1535	0·2067	0·2069	0·0002+
150	40	"	"	2·6554	0·2560	0·2549	0·0011—
175	35	"	"	3·2428	0·3110	0·3118	0·0008+
"	35	"	"	3·2428	0·3085	0·3083	0·0002—

Obviously the reduction of selenious acid by this method is regular and accurate.

When similar treatment was applied to selenic acid it became apparent that the arsenic acid attacked and destroyed the iodide before the selenic acid had been completely reduced. It is plain, therefore, that the selenic acid must be reduced to the condition of selenious acid before its estimation by the iodide method can be attempted. Ordinarily the simplest mode of reducing selenic acid is by boiling it in solution with hydrochloric acid of definite strength,* but in this case the presence of hydrochloric acid is precluded on account of the consequent volatilization of arsenious chloride during the process of concentration in the subsequent treatment with the iodide. It has been shown, however, in a recent paper from this laboratory† that selenic acid is easily and completely reduced to selenious acid by potassium bromide and sulphuric acid under defined conditions. Moreover, arsenious bromide is not volatilized appreciably under the conditions. We made the attempt, therefore, to effect the iodometric determination of selenic acid by first reducing it to selenious acid by the bromide process and then treating the residue with arsenic acid and potassium iodide in the manner described.

Selenic acid was prepared in standard solution by treating a known weight of pure resublimed selenium dioxide by a strong solution of potassium permanganate, in presence of a moderate amount of sulphuric acid, until the purple color was distinctly visible, dissolving the precipitated oxide of manganese by oxalic acid, again adding permanganate until the final color of faintly visible pink was permanent for a half-hour or more, and diluting to a fixed volume. Portions of the solution of selenic acid were measured into counterpoised Erlenmeyer flasks of 300 cm^3

* Gooch and Evans, this Journal, l. 400.
† Gooch and Scoville, this Journal, l. 402.

capacity and weighed, 1 grm. of potassium bromide was added, and sulphuric acid in such quantity that the total amount of the free acid should correspond to 20 cm^3 of the acid of half-strength. The solution possessing a volume of 60 cm^3 to 100 cm^3 was boiled until the clear, colorless solution left when the bromine vanished began to color again. Experience showed that the reappearance of the brownish color is very easily seen and that it is not safe to conclude that all free bromine has been eliminated, under the conditions of dilution and proportion, until this stage of concentration—which corresponds to a volume of about 35 cm^3—has been reached; but the distillation should not be pushed beyond the point at which the returning color is noted. When this condition was reached the solution was cooled, and treated exactly in the manner described for the reduction of selenious acid. The neutralization by acid potassium carbonate, after the final boiling, generally occasioned the precipitation of manganous carbonate, but the precipitate did not interfere in the slightest with the titration which followed.

The following table comprises the determinations which were made to test the accuracy of the iodometric determination of selenic acid by the combined processes of reduction.

SeO_2 taken as H_2SeO_4. grm.	KI used in second reduction. grm.	SeO_2 found. grm.	Error grm.
0·0378	0·6306	0·0380	0·0002 +
0·0378	0·5643	0·0374	0·0004 --
0·0516	0·7136	0·0517	0 0001 +
0·0503	0·7302	0·0508	0·0005 +
0·0541	0·6671	0·0544	0·0003 +
0·1007	1·3277	0·1011	0·0004 +
0·1008	1·3277	0·1011	0·0003 +
0·1007	1·2082	0·1005	0·0002 —
0·1007	1·1684	0·1016	0·0009 +
0·1007	1·0522	0·0999	0·0008 —
0·1009	1·2679	0·1005	0·0004 —
0·1031	1·1119	0·1032	0·0001 +
0·1870	1·8720	0·1879	0·0009 +
0·2014	1·9915	0·2020	0·0006 +
0·2016	2·0745	0·2025	0·0009 +
0·2059	1·8687	0·2064	0·0005 +

It is plain, therefore, that selenic acid may be determined iodometrically with accuracy by first reducing it to the condition of selenious acid by treatment with potassium bromide in presence of sulphuric acid, in the manner described, and then completing the reduction to the elementary condition by the treatment with potassium iodide and potassium arseniate.