

ART. XIX.—*A method for the Determination of Antimony and its condition of Oxidation*; by F. A. GOOCH and H. W. GRUENER.

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

BUNSEN'S method of determining qualitatively the condition of oxidation of salts of antimony, by boiling these substances in solution with potassium iodide and hydrochloric acid and noting whether the liquid takes the color of free iodine, has been applied successfully to the quantitative determination of antimony in its highest condition of oxidation by Weller,* who distils the iodine from the solution, collects it in the distillate and, determining it volumetrically, calculates from the amount of it found the antimonie salt which sets it free according to the equation



The advantage of treating the residue, rather than the distillate, in analytical processes in general which involve distillation is so obvious as to constrain us to seek conditions under which Bunsen's reaction may be applied in such manner that the antimony shall be held and estimated directly in the residue. The general plan of work was laid down in a similar process elaborated in this laboratory for the reduction of arsenic acid.† According to this process the arsenic to be reduced is taken in a solution of appropriate dilution, and treated with sulphuric acid in adjusted amount and an excess of potassium iodide. The liquid thus prepared is boiled to a definite degree of concentration, the iodine then remaining unexpelled, if any, is bleached by the very careful addition of dilute (centinormal) sulphurous acid, and the liquid is immediately diluted and neutralized. After cooling, the reduced arsenic is titrated by standard iodine in presence of starch.

We found in preliminary experimentation that the same general plan of treatment is available in the handling of antimonie compounds, but it is necessary to take precautions to prevent the deposition of the antimony from solution upon the addition of the sulphuric acid. Tartaric acid accomplishes this effect satisfactorily and does not, as the result proved, introduce undesirable complications. It transpired also that the dilution of the solution at which the crystalline iodide or oxyiodide separates out during the boiling is greater than is the case when similar amounts of arsenic are dealt with. It appeared, for example, that concentration to 45cm.³ was sufficient to cause crystallization and slight sublimation when the

* Ann. d. Chem. u. Pharm., ccxiii, 246.

† Gooch and Browning, this Journal, xl, p. 66.

amount of antimonious oxide present (with excess of potassium iodide and 10cm.³ of sulphuric acid, 1:1) was approximately 0.2 grm. Otherwise the process as employed in the reduction of arsenic appeared to be applicable to the similar treatment of antimony.

The following quantitative experiments were undertaken to discover the condition of concentration best suited to the reduction of antimonious salts under circumstances otherwise like those adapted to the reduction of arsenic, and to test the perfection of the process. Definite amounts of tartar emetic, purified by recrystallization, were used to make the antimonious salt to be afterward reduced, the antimony being raised to the highest degree of oxidation by titration with standard iodine after the addition of sodium tartrate (to prevent the precipitation of the antimony during the process of oxidation) and hydrogen sodium carbonate in the usual excess. In this process starch was sometimes employed to give the end reaction, and sometimes reliance was placed upon the appearance of the color of free iodine, experience having indicated that the use of the starch is not essential when the solutions are sufficiently small in volume, though as a matter of course, the correction demanded for the excess of iodine necessary to give color to the body of liquid is greater when starch is not used.

This treatment of the tartar emetic served the double purpose of providing a perfectly definite antimonious salt and re-standardizing the solution of standard iodine, which was to be used subsequently in reoxidizing the antimony after its reduction, against the tartar emetic; and thus the imperfection of the process, whatever it may be, whether in the reduction or elsewhere, becomes apparent and is measured immediately by the difference between the amounts of iodine employed in the two oxidations. This mode of standardizing the iodine appears to be peculiarly advantageous in view of Fresenius's demonstration* that the iodometric estimation of antimony yields too high results, at least in the case of tartar emetic, when the standard iodine is standardized in the usual manner and, as is undoubtedly best, the characteristic starch-blue is taken for the end reaction rather than the premonitory and somewhat indefinite reddish tint.

The larger amounts of tartar emetic were weighed out dry; the smaller quantities were secured by measuring out definite portions of a solution of fixed strength. To every portion was added, in an Erlenmeyer beaker of 300 cm.³ capacity, one gram of tartaric acid previously treated with an excess of hydrogen sodium carbonate, and the oxidation was effected, as described, by iodine dissolved in potassium iodide to a solution

*Quant. Anal. 6^{te} Aufl., 817.

approximately decinormal. Four grams of tartaric acid were added, and dilute sulphuric acid, if the solution still remained alkaline, to faint acidity. In addition 10 cm.³ of a mixture of sulphuric acid and water in equal parts were introduced, and the liquid was boiled after introducing a platinum spiral to prevent bumping, and a trap made of a two-bulb drying tube cut short and hung, large end downward, in the mouth of the flask, to prevent mechanical loss. At the chosen degree of concentration, determined by marks upon the flask, the boiling was stopped, the color bleached by the cautious addition of sulphurous acid (approximately centinormal), and the solution, nearly neutralized with sodium hydrate, made alkaline by hydrogen sodium carbonate added in an excess amounting to about 20 cm.³ of the saturated solution, was titrated with the standard (decinormal) iodine after the addition of a fresh portion of starch.

Table I, contains the account of experiments in which the larger amounts of antimony were employed.

TABLE I.

Final volume.	Tartar emetic taken.	Sb ₂ O ₃ taken.	Iodine used in final oxidation.	Sb ₂ O ₃ found.	Error.
cm. ³	gram.	gram.	gram.	gram.	gram.
100	0.5021	0.2178	0.3522	0.2004	0.0174—
80	0.5030	0.2181	0.3784	0.2153	0.0028—
60	0.5008	0.2172	0.3768	0.2144	0.0028—
60	0.5010	0.2173	0.3780	0.2151	0.0022—
60	0.5010	0.2173	0.3809	0.2168	0.0005—
55	0.5023	0.2178	0.3827	0.2178	0.0000
55	0.5015	0.2175	0.3806	0.2166	0.0009—
50	0.5007	0.2172	0.3814	0.2171	0.0001—
50	0.5039	0.2185	0.3839	0.2185	0.0000
45	0.5001	0.2169	0.3818	0.2173	0.0004+
45	0.5004	0.2170	0.3825	0.2176	0.0006+

The results of these experiments indicate unmistakably that complete reduction may be brought about under the conditions, but that concentration to a volume of from 45 cm.³ to 55 cm.³ during the boiling is not only advantageous but necessary. The mean error of the determination in which the final volume fell within these limits was zero between limits of 0.0009 gm. — or 0.0006 gm.+. In both determinations in which a final volume of 45 cm.³ was reached, and in one of the experiments in which the final volume was 50 cm.³, the formation of the crystalline antimonious iodide or oxyiodide in the liquid was noted, and the deposition of a very slight sublimate of the same salt in the trap. It is evident, therefore, that it would be hazardous to attempt to push the concentration further.

In all these experiments hydriodic acid was present in amount equivalent to 1.1 grm. of potassium iodide—0.5 grm. introduced as iodine and 0.6 grm. introduced as such in the standard iodine where it plays the part of solvent.

In the experiments recorded in Table II, smaller amounts of antimony and correspondingly smaller quantities of the oxidizing solution were employed; otherwise, the same general mode of proceeding was followed. The limits of concentration fixed upon were, however, varied somewhat. The previous experiments showed plainly that anything like a complete reduction of the antimony could not be anticipated when the final volume was greater than 60 cm.³, and the experience with the smaller amounts of antimony treated in the second series pointed to the fact, as the work progressed, that for them the crystallization and sublimation did not occur until the concentration had brought about a decrease in volume to 35 cm.³. The limits of final volume were placed therefore, for these experiments, at 60 cm.³ and 35 cm.³. Centinormal iodine was used for the oxidations and bleaching with sulphurous acid was found to be unnecessary, the amount of iodine liberated in these experiments being so small as to vanish in the concentration so completely that no color was visible (nor was it brought out by starch) after washing down the trap and cooling. There did remain a trace of color before the addition of the water but this seemed to us to be due in all probability to the incipient formation of the antimonious iodide or oxyiodide which is decomposed by the action of more water. At all events it disappeared on the addition of water and no reoxidation of the antimony was found subsequently.

TABLE II.

Final Volume.	Tartar Emetic taken.	Sb ₂ O ₃ taken.	Iodine used in final oxidation.	Sb ₂ O ₃ found.	Error.
cm. ³ .	grm.	grm.	grm.	grm.	grm.
60	0.0500	0.0217	0.0239	0.0136	0.0081—
60	0.0500	0.0217	0.0258	0.0147	0.0070—
60	0.0500	0.0217	0.0261	0.0148	0.0069—
50	0.0500	0.0217	0.0316	0.0180	0.0037—
40	0.0500	0.0217	0.0385	0.0219	0.0002+
35	0.0500	0.0217	0.0380	0.0216	0.0001—
35	0.0500	0.0217	0.0381	0.0217	0.0000
35	0.0500	0.0217	0.0382	0.0218	0.0001+
35	0.0500	0.0217	0.0382	0.0218	0.0001+

These results show that for the smaller amounts of antimony the reduction was completed only by pushing the degree of concentration somewhat lower than was found to be necessary

in treating the larger amounts. The only point in which these experiments differ essentially from those of the previous series is in the quantity of the iodine solution employed to effect this oxidation. So far as concerns the free iodine itself the conditions are similar in both series; for the iodine is converted in both cases to hydriodic acid exactly equivalent in amount to the antimony acted upon. The potassium iodide which is added in the iodine solution produces by action upon the sulphuric acid present an excess of hydriodic acid, which is, of course, dependent upon the absolute amount of the iodine solution employed. The hydriodic acid is the active agent in the reduction of the antimony, and to the greater mass-action in the former series of experiments might be attributed the more complete reduction for equal degrees of concentration. Accordingly the determinations of Table III were made to put this point to the test. In these experiments the conditions were identical with those of the determinations of Table II, excepting that in every case 1 grm. of potassium iodide was added to the liquid before boiling, thus bringing the total amount of hydriodic acid present to an equality with that present in the experiments of Table I, in which the larger amounts of antimony were treated. The results of these experiments bear out completely the hypothesis concerning the mass-action of the hydriodic acid—the smaller amounts of antimony being completely reduced in the presence of the large excess of hydriodic acid even at a final volume of 60 cm.³ with a maximum error of 0·0002 grm.—

TABLE III.

Final Volume.	Tartar Emetic taken.	Sb ₂ O ₃ taken.	Iodine used in final oxidation.	Sb ₂ O ₃ found.	Error.
cm. ³	grm.	grm.	grm.	grm.	grm.
60	0·0500	0·0217	0·0378	0·0215	0·0002—
60	0·0500	0·0217	0·0379	0·0216	0·0001—
60	0·0500	0·0217	0·0379	0·0216	0·0001—

It is plain therefore that we have in the phenomena described the basis of a good method for the iodometric determination of the condition of oxidation of antimony; for, the amount of antimonious salt present in a mixture of antimonious and antimonie salts may be determined by direct titration in alkaline solution, and the total amount of antimony present is given similarly after the treatment by boiling, as described, with potassium iodide and sulphuric acid, the amount of antimonie salt being immediately calculable from the difference between the quantities of the standard iodine used as the

oxidizer before and after reduction. The best method of proceeding appears to be that in which the concentration was restricted so that the point of sublimation and crystallization was not reached and in which the presence of an excess of potassium iodide was assured.

It seemed desirable, in this connection, to test the applicability of the method, as outlined, to the reduction and estimation of antimony and arsenic associated together, as so often happens in practice. The preceding experiments establish the fact that it is undesirable to attempt, in treating antimony, to force the concentration of the solution below 50 cm.³, under the conditions laid down and when the amount of antimony present is equivalent to the maximum with which we have experimented, about 0.2 gm. of antimonious oxide. In the parallel process for the determination of arsenic concentration to 40 cm.³ was recommended in all cases (the maximum amount treated being equivalent to about 0.33 gm. of arsenious oxide), but it was not shown in the elaboration of that process that reduction would not take place at a concentration not quite so extreme. In the results recorded in Table V, which relate to experiments which duplicate the conditions found most favorable to the reduction of varying amounts of antimony,—the presence of the equivalent of 1.1 gm. of potassium iodide, and concentration to 50 cm.³—and differ from these only in the fact that arsenic was associated with antimony in every case, it appears that the reduction of arsenic may be effected simultaneously with that of the antimony.

TABLE IV.

Final Volume.	Tartar Emetic taken.	Sb ₂ O ₃ taken.	As ₂ O ₃ taken.	Iodine used in first oxidation.	Iodine used in final oxidation.	Difference between the amounts of iodine used in the two oxidations.	Error in terms of	
							Sb ₂ O ₃	As ₂ O ₃ .
cm. ³	gram.	gram.	gram.	cm. ³	cm. ³	cm. ³	gram.	gram.
50	0.1530	0.0870	0.0500	19.37	19.43	0.06 +	0.0004 +	0.0003 —
50	0.1503	0.0855	0.0495	19.05	19.02	0.03 —	0.0002 —	0.0001 —
50	0.1503	0.0855	0.0544	20.05	19.97	0.08 —	0.0006 —	0.0004 —
50	0.1503	0.0855	0.0495	19.05	19.00	0.05 —	0.0004 —	0.0003 +

It is plain that the error in these results, whether reckoned as falling upon the antimonious oxide or upon the arsenious oxide, is quite within the limits allowable in volumetric determinations by means of decinormal solutions. One point, however, in the determination of the combined amounts of antimony and arsenic by the method here proposed deserves special consideration. It has been shown in the work to which reference has been made that arsenic is reducible by the pro-

cess outlined and determinable with accuracy by titration with iodine standardized against arsenious oxide. In this later work we show that antimony may be reduced similarly and estimated satisfactorily by titration against iodine standardized against tartar emetic. These two methods of standardizing do not yield identical results, and so we are confronted with an inherent error in the process for estimating antimony and arsenic at once, which cannot be overcome unless the individual amount of one or other constituent may be otherwise determined. If the determination of either the arsenic or antimony is possible it is, of course, easy to calculate with the use of the appropriate standard the amount of the solution of iodine which is really engaged in the oxidation of this particular constituent, and the remainder of the iodine actually employed, gauged by the second standard, will give the corrected amount of the second constituent.

In case no such correction is feasible it becomes a matter of interest to note the magnitude of possible error. Our experience, based upon many determinations throughout the course of the work detailed above, pointed to a difference in the value of the two standards amounting to about one-half of one per cent. If, therefore, the weight of reduced oxide amounts to the maximum which we have experimented with—about 0.2 grm.—the greatest possible error will be 0.0010 grm. + or 0.0010 grm. —, according as the entire 0.2 grm. is antimonious oxide estimated by the arsenic standard, or arsenious oxide estimated by the tartar emetic standard. The essential features of the process which we propose for the reduction of antimony and the determination of its degree of oxidation are recapitulated briefly in the following statement.

The salt of antimony, not exceeding the equivalent of about 0.2 grm. of antimonious oxide, is titrated, in presence of 1 grm. of sodium tartrate and the usual excess of sodium hydrogen carbonate, by means of iodine standardized against tartar emetic. The result of this titration gives the amount of antimonious salt present. To the solution are then added 4 grms. of tartaric, dilute sulphuric acid, if necessary, to neutralization, an excess of 10 cm.³ of half and half sulphuric acid, and enough potassium iodide so that there shall be present of hydriodic acid the equivalent of a little more than 1 grm. of the iodide. The liquid is diluted to 100 cm.³, boiled in an Erlenmeyer beaker until the volume is decreased to 50 cm.³, the precaution being taken to introduce a platinum spiral to prevent bumping and a trap, as described, to obviate mechanical loss. The color remaining after concentration, if there be any, is bleached by dilute sulphurous acid (approximately centinormal). The solution is nearly neutralized with

sodium hydrate, treated with an excess of sodium hydrogen carbonate amounting to 20 cm.³ of the saturated solution, cooled, and titrated in presence of starch by the standard iodine. This final titration gives, of course, the entire amount of antimony present. The difference between the indications of the two titrations is the measure of the antimony in the higher condition of oxidation. The method as outlined is accurate and rapid, and so simple as regards manipulation that a number of determinations can be carried through simultaneously with the use of ordinary apparatus.