ART. XV.—*Revision of the Atomic Weight of Antimony;* by JOSIAH P. COOKE, Jr.

(Concluded from page 49.)

AFTER a long series of experiments, which threw but little light on the cause of the discrepancy that had now become so prominent, although they yielded very interesting subsidiary results which are described in detail in the original paper, we made a series of analyses of antimonious bromide with the hope that if there was, as we suspected, a source of constant error in the analyses of antimonious chloride, the same influence would affect the analyses of the corresponding bromide to a different degree and might thus reveal its nature.

* Arch. des Sciences, lviii, 293, March, 1877.

We prepared the bromide of antimony by adding in small portions at a time the pulverized metal to a strong solution of bromine in sulphide of carbon. The retort containing the solution was kept cool by snow, and shaken after each addition until the action ceased. As soon as the color of bromine was discharged, the sulphide of carbon was distilled off over a water bath; and then, replacing the water bath with a gas lamp, the bromide of antimony was first boiled, and then distilled over the finely powdered antimony which had been added in excess. On account of the high boiling point of bromide of antimony, and the readiness with which its vapor condenses, it was found best in distilling to cover the body of the retort with a hood. The bromide thus prepared was purified by repeated distillations over pulverized antimony, as in the case of the chloride, and finally by crystallizing and recrystallizing several times from solution in purified sulphide of carbon. A warm saturated solution in sulphide of carbon deposits, when cooled to the freezing point, the greater part of the bromide of antimony in fine acicular crystals. These crystals were dried first with blotting-paper, and then *in vacuo* over sulphuric acid. The antimonious bromide thus purified by fractional distillation and crystallization was only a very small fraction of the first crude product. It was pure white, had a high silky luster, and, when first made, was wholly destitute of odor. It was carefully examined for chlorine, iodine, and arsenic; but the delicate tests which we possess for all three of these elements so frequently associated with commercial antimony and bromine, failed to show the least trace of either in the bromide of antimony we analyzed. The determinations of bromine were made in all respects like those of chlorine. Great care was taken not to add more than a very slight excess of argentic nitrate, and we found that under these conditions the supernatant liquid cleared more readily above the precipitate in the case of bromide of silver than with the corresponding chloride, and for this reason the first could be washed more quickly than the last. The results of these determinations are embodied in the table on the following page.

Here, as before, the letters indicate different preparations: *a* was made and purified as described above; *b* was the same material as *a* redistilled and again crystallized from bisulphide of carbon; *c* was another portion of the same material several times redistilled and twice recrystallized from the same solvent; *d* was a separate preparation from the start; *e* was another separate preparation purified with extreme care. In the last case there was over a kilogram of the crude product, which was reduced by the fractional distillation and crystallization—each process repeated from ten to twenty times—

to the few grams used in the analyses. These methods of purifying the substance were thus pushed to their utmost limits.

ANALYSES OF ANTIMONIOUS BROMIDE.

DETEMINATION OF BROMINE.

No.	Wt. of $SbBr_3$ taken in grams.	Wt. of AgBr obtained.	% of Bromine Br=80, Ag 108.
1, *a.*	1·8621	2·9216	66·765
2, *a.*	0·9856	1·5422	66·584
3, *b.*	1·8650	2·9268	66·779
4, *b.*	1·5330	2·4030	66·703
5, *b.*	1·3689	2·1445	66·663
6, *c.*	1·2124	1·8991	66·655
7, *c.*	0·9417	1·4749	66·647
8, *d.*	2·5404	3·9755	66·593
9, *d.*	1·5269	2·3905	66·623
10, *e.*	1·8604	2·9180	66·743
11, *e.*	1·7298	2·7083	66·624
12, *e.*	3·2838	5·1398	66·604
13, *e.*	2·3589	3·6959	66·671
14, *e.*	1·3323	2·0863	66·635
15, *e.*	2·6974	4·2285	66·708

Mean value from last six determinations,	66·664
Mean value from all the determinations,	66·6665
Theory Sb 120 requires,	66·6666
Theory Sb 122 "	66·2983

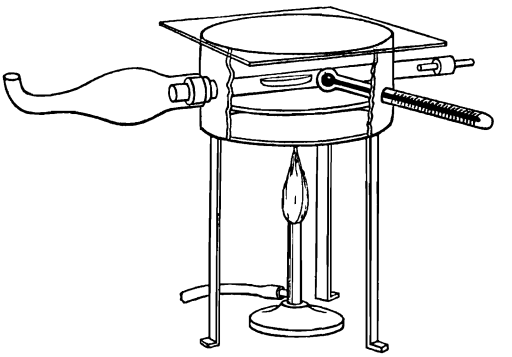
If in calculating the result of the above bromine determinations we use the atomic weights of Stas,—Br=79·952, Ag=107·93,— the per cents found will be in each case only 0·002 higher, which is, of course, an inappreciable difference. Hence, whether we take Stas's or Dumas's values for the atomic weights of bromine and silver, the atomic weight of antimony deduced from the above determinations is exactly 120·00.

This is certainly a remarkably close confirmation of our previous conclusion. Indeed the wonderful coincidence between the observed and the theoretical results must be to a certain extent accidental; for no process of chemical analysis is capable of the accuracy which this agreement would imply. Still it should be noticed that the probable errors of the process, so far as they are indicated by the variations from the mean value, are not larger than we might expect would be eliminated by multiplying observations; and, further, that the mean of the last six determinations which are undoubtedly the most trustworthy, is nearly as close to the theory as the mean of the whole.

But not only did these experiments on bromide of antimony thus confirm our previous conclusion: they also gave the first definite clew to the explanation of the disagreement with otherwise consistent results which our experiments on chloride of antimony had presented. The one difference between the chloride and the bromide, which appeared to render the last better suited to yield accurate results, was the difference in their hygroscopic qualities. As we have stated, the chloride is one of the most hygroscopic substances known. The bromide is also hygroscopic, but far less so, presenting no unusual difficulties of manipulation; and, since our tests indicated that both substances were otherwise pure, we at once drew the inference that the different results we had obtained with chloride of antimony must depend on the extraordinary attraction of this substance for moisture. Before, however, fully following out the clew thus obtained, we made a similar study of the iodide of antimony.

The iodide of antimony was prepared like the bromide, by shaking up in a glass flask a solution of iodine in bisulphide of carbon with finely pulverized metallic antimony. On filtering and decanting, after the color of the iodine is discharged, a solution having a pale greenish-yellow color is obtained, from which on cooling or on evaporation red crystals of iodide of antimony are deposited. The substance may be purified by recrystallization from the same solvent; but iodide of antimony is far less soluble in bisulphide of carbon than the chloride or bromide, and cannot therefore be so advantageously treated in this way, nor can the small amount of carbonaceous impurity which the crystals acquire from the solvent be so easily removed. Moreover, iodide of antimony cannot be so readily distilled as the chloride or bromide, on account of its high boiling point, which is above that of metallic mercury. But another property of iodide of antimony which, so far as we know, has not hitherto been noticed, interferes still more seriously with these methods of purifying this substance. In all its conditions, it undergoes a more or less rapid oxidation in contact with atmospheric air, forming oxi-iodide of antimony (SbOI) and free iodine. When iodide of antimony is rapidly boiled in a small flask, so that the body and most of the neck are kept full of vapor at the boiling-point, the action at the surface of contact of the vapor and the air is very striking; iodine is set free in vapor, with its familiar violet color, while the oxi-iodide is precipitated in clouds, forming a most beautiful phenomenon. So also when the greenish-yellow solution (above described) of the iodide in bisulphide of carbon is exposed to the air and light, it rapidly becomes colored red from the liberation of iodine, and at the same time turbid from the

deposition of the insoluble oxi-iodide. Even the crystals of iodide of antimony, when kept in the light, slowly become opaque from the formation of the same oxi-iodide; while the odor and staining of the stopper of the bottle furnish abundant proof of the liberation of iodine. The study of these phenomena was most interesting, and the results obtained will be described in another paper. It is sufficient for the present to say that they pointed out to us a great source of impurity in iodide of antimony, and fully explained the want of accordance in our analyses of the crystals of this substance as first pre-



pared. It was evident that we could only hope to purify the material by distilling or subliming it in an atmosphere of inert gas; and we devised the apparatus represented in the accompanying figure for this purpose, which we have since found very generally useful for all sublimations where the temperature required does not exceed that which can be measured with a mercury thermometer. The apparatus has been already referred to, and requires no further description. It was a simple modification of the apparatus used before for drying at a regulated temperature the precipitates of sulphide of antimony, which, as we have stated, was so arranged that the character of any sublimates which might be given off could be observed. We used the same glass tube passing through the sheet-iron air-bath, with its transparent mica cover, only we added a common glass adapter, selected so that its mouth just fitted over the open end of the tube. A platinum nacelle containing iodide of antimony, which had already been purified by crystallization, was placed in the tube within the air-bath, but near the open mouth; and, while a current of dry carbonic dioxide through the apparatus was steadily maintained, the air-bath was heated by a gas lamp to the required temperature which was indicated by a thermometer as shown in our figure. Iodide of antimony is sensibly volatile, even at 100°; and long before

it reaches its melting point, 167°, the evaporation becomes very marked. As soon as melted, it sublimes quite rapidly; and we obtained the best results by keeping the temperature between 180° and 200°, and by shifting the adapters we used as receivers, it was easy to collect the different portions of the sublimate. We thus obtained crystals of two isomeric modifications of iodide of antimony: the more abundant in large hexagonal plates, often half an inch or more in diameter, perfectly transparent, and of the most brilliant ruby-red color; the other in small rhombic plates, having the same peculiar greenish-yellow color as the solution of the iodide already mentioned. The amount of the last was always small, but it was larger in proportion as the temperature was lower. This new and most interesting product will be described in the paper just referred to. Of these crystals, the most brilliant, chiefly of the red variety, were selected for analysis. The iodine determinations were conducted in all respects like those of chlorine and bromine. The iodide was first dissolved by a very concentrated solution of tartaric acid, and then the solution was diluted to the required extent. The same care was taken not to add more than a very slight excess of argentic nitrate, and the amount required was accurately weighed out in each case. Each of the determinations was made with a separate preparation in so far as it was a product of a separate sublimation; but the material sublimed was essentially the same in all cases, —a mixture of the products of many crystallizations from the crude material made as described above. The results are collected in the following table:

ANALYSIS OF IODIDE OF ANTIMONY.

IODINE DETERMINATIONS.

No.	Wt. of SbI_3, grams.	Wt. of AgI, grams.	% of Iodine, I=127, Ag=108.	Variety.
1.	1·1877	1·6727	76·110	Pure red.
2.	0·4610	0·6497	76·161	Chiefly yellow.
3.	3·2527	4·5716	75·956	Pure red.
4.	1·8068	2·5389	75·939	Pure red.
5.	1·5970	2·2456	75·990	Red and yellow.
6.	2·3201	3·2645	76·040	Pure red.
7.	0·3496	0·4927	76·161	Chiefly yellow.

Mean value ..... 76·051
Theory Sb=120, requires ..... 76·047
Theory Sb=122, " ..... 75·744

If in calculating the results of these iodine determinations we use the atomic weights of Stas, I=126·85 and Ag=107·93, the mean value would be 76·034, and the corresponding atomic weight of antimony 119·95.

The difference (0·004) between the first mean value and theory—corresponding to only about $\frac{2}{170}$ of a milligram in the largest amount of argentic iodide weighed—is evidently insignificant, so that these results confirm the lower value of the atomic weight of antimony as closely as did the analyses of the bromide.

As we have already intimated, our analyses of the iodide of antimony, as first crystallized from bisulphide of carbon, yielded very discordant results. These we give in the table below, not, as before, in the exact order in which the analyses were made, but in the order of the several values, so as to exhibit the distribution of the errors.

ANALYSES OF CRYSTALLIZED ANTIMONIOUS IODIDE, RED VARIETY.

No.	% of Iodine.
1	75·71
2	75·76
3	75·78
4	75·80
5	75·84
6	75·85
7	75·87
8	75·89
9	75·94
Mean value	75·83
Theory Sb=122	75·74
Theory Sb=120	76·05

The cause of this discordance we attributed, as we have intimated, chiefly to the remarkable readiness with which iodide of antimony undergoes oxidation in contact with the air, resulting in the formation of oxi-iodide of antimony and free iodine, thus:—

$$2SbI_3 + O{=}O = 2SbOI + 2\,I\text{-}I.$$

While the free iodine escapes, the oxi-iodide remains as an impurity in the preparation, and the effect is a replacement of a portion of its iodine by oxygen. Now, since eight parts of oxygen replace one hundred and twenty-seven parts of iodine, it can readily be seen that an otherwise almost imperceptible amount of oxidation would be sufficient to produce all the variation from the normal composition which the above results present. A simple calculation will show that an absorption of only $\frac{4}{10}\frac{7}{00}$ths of one per cent of oxygen, or less than half a milligram by each gram of iodide of antimony, would reduce the per cent of iodine from the theoretical value, 76·047, to the mean of the above results,

75·832; and that a corresponding absorption of three-quarters of a milligram would reduce the per cent to 75·700, the lowest observed. It is not, therefore, surprising that we could obtain concordant results only with material which had been both purified by crystallization and also *recently* sublimed.

Returning now to discuss again the cause of the disagreement of the analyses of antimonious chloride with our otherwise consistent results in regard to the atomic weight of antimony, it was obvious that the strong hygroscopic power of the chloride must lead to a replacement precisely similar to that which is produced in the iodide by direct oxidation; for, as we have before said, the crystals of antimonious chloride cannot be exposed to the atmosphere for an instant without absorbing a perceptible amount of moisture, and every molecule of water thus absorbed reacts on a molecule of the chloride, thus:—

$$SbCl_3 + H_2O = SbOCl + 2HCl.$$

And when the antimonious chloride is boiled, the hydrochloric acid formed is given off, while the oxichloride remains behind, dissolved in the great mass of the liquid. Indeed, it seems impossible, with our ordinary appliances, to prepare or purify antimonious chloride without its becoming contaminated with oxichloride; and our experiments would indicate that when once it has been formed, as above described, in the mass of the material, it cannot be wholly removed by distillation or crystallization, however often these processes may be repeated.

Naturally, our attention was very early called to this obvious source of impurity in the antimonious chloride we prepared: and we noticed from the first that, even after the material had been many times distilled, there was always left, on repeating the process, a very small amount of dark-colored residue. We had examined the residue, and found that it was a mixture of chloride and oxichloride of antimony, colored by a trace of carbonaceous material; and we had made a long series of analyses for the purpose of studying the effect produced by the action we have described. The result of these analyses is given in the following table. We started with material already purified by fractional distillation and crystallization, and distilled it ten times in succession; not, however, carrying the distillation to absolute dryness, but leaving, so far as we could judge by the eye, about the same amount of residue in the retort each time. These residues we analyzed, as we did also the final distillate. The material first distilled was the same as that marked *c* in the table on page 47, and we assumed that the average of the results there given truly represented its composition.

ANALYSES OF ANTIMONIOUS CHLORIDE.

RESIDUES AND DISTILLATES.

	% of Chlorine.
The original purified preparation	46·64
The residue of 1st distillate	45·71
" 2d "	45·66
" 3d "	46·03
" 4th "	46·26
" 5th "	46·26
" 6th "	46·00
" 7th "	46·03
" 8th "	45·94
" 9th "	45·65
" 10th "	45·99
The last distillate	46·62

Although, under the circumstances, we could not expect great precision, yet it was evident from these analyses that the amount of impurity in the residues was not diminished by the successive distillations; and we therefore concluded that additional oxichloride of antimony must be formed each time during the very short contact with the atmosphere which the transfers between the several distillations necessarily involved. But, on the other hand, the very remarkable fact that these ten distillations produced no sensible change in the composition of the great mass of the material seemed to indicate equally clearly that this action of the atmosphere had no perceptible influence on the final result; and this opinion was still further strengthened when, on twice distilling portions of the last distillate, at a low temperature, in a current of dry hydrogen, we obtained products given again—very nearly at least—the same per cent of chlorine. And, lastly, when to all this evidence were added the results of the complete analysis of the chloride, showing an amount of antimony which fully supplemented the very constant per cent of chlorine, the assumption that any material amount of impurity could be present appeared wholly untenable. Yet we have seen how this assumption was forced back upon us by the subsequent results of the investigation.

Returning to the subject after our experiments with iodide of antimony, we, for the first time, fully appreciated how very small an amount of oxygen—the only real impurity present—was required to reduce the per cent of chlorine in antimonious chloride from 47·02, the amount corresponding to Sb=120, to 46·61, which corresponds to Sb=122; for, while the effect is so differently produced, yet the result of the action of the atmosphere on the chloride of antimony is wholly like that of its action on the iodide. It ends in replacing a small amount of chlorine by oxygen; and although, in consequence of the

smaller atomic weight of chlorine, it requires in this last case a larger replacement to produce a corresponding change of percentage composition, yet still the amount required to make all the difference in question is very small; so that, when we come to sum up the supposed completed results (as on page 47), it might easily be covered up by slight inaccuracies of the analytical work. An easy calculation will show that the substitution of but $\frac{146}{1000}$ of one per cent of oxygen for the equivalent amount of chlorine would reduce the per cent of this last element in the chloride from 47·020, corresponding to Sb=120, to 46·608, which corresponds to Sb=122; and such a substitution would result from the absorption of only $1\frac{6}{10}$ milligram of water by each gram of the chloride. The composition of the material would then be as follows:—

COMPOSITION OF ANTIMONIOUS CHLORIDE WITH $\frac{146}{1000}$ PER CENT OF O WHEN Cl=35·5 AND Sb=120.

Chlorine	46·608
Oxygen	·146
Antimony	53·246
	100·000

Now it will be seen by referring to the tables, on pages 47 and 48, that these percentages do not differ from the mean of the results of our previous analyses as much as these results differ among themselves; and we therefore determined to repeat these analyses, hoping that the experience we had acquired in both chlorine and antimony determinations would now enable us to obtain results sufficiently sharp to show even the small differences of composition which the substitution in question would produce.

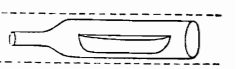
Meanwhile, we instituted a series of experiments with a view of studying the decomposition which the oxichloride of antimony undergoes under the action of heat, in the hope that we might thus discover some method by which the amount of oxichloride of antimony in our preparations might be directly determined. For this purpose, we used first crystallized SbOCl, obtained by the action of alcohol on chloride of antimony in a sealed tube, which we weighed out into a platinum nacelle, and heated to various regulated temperatures, using for this purpose the apparatus already described. It appeared that the decomposition took place in two stages. The first stage of the decomposition began between 167° and 175°, but was not completed until between 260° and 280°. The second stage began at about 320°, but required for its completion a red heat. During both stages, chloride of antimony sublimed; and there was left in the nacelle at the close of the process beautiful crystals

of Sb_2O_3. In another experiment, we used crystallized $Sb_4O_5Cl_2$, prepared in the same way as the SbOCl, but with different proportions of alcohol and chloride of antimony. In this case, the decomposition did not begin until 320°, but in other respects both the process and the products were as in the first experiment. It was quite evident that the chemical changes which took place in the two stages of decomposition we have noticed were represented by the following reactions:

First stage: $5SbOCl = Sb_4O_5Cl_2 + SbCl_3$; (1)

Second stage: $3Sb_4O_5Cl_2 = 5Sb_2O_3 + 2SbCl_3$; (2)

but the relative weights observed in the first two experiments were of no value, because it was evident that a no inconsiderable amount of Sb_2O_3 was lost by sublimation. Since, however, the small sublimate of oxide condensed in the glass combustion-tube very much nearer the nacelle than the very much larger sublimate of chloride, we varied the apparatus in our third experiment so far as to place the nacelle in a tube of the shape represented in the accompanying figure. This tube was weighed with the nacelle, and was so selected that it quite closely fitted the combustion-tube within which it was placed for heating, as shown in figure by dotted lines. And it is evident that, while with this arrangement the $SbCl_3$ would be swept by the CO_2 gas into the colder portion of the combustion-tube, the greater part at least of the sublimed oxide would be retained in the small tube, which was of course at each stage weighed with the nacelle, as at first. Our results were as follows:—



Weight of SbOCl	0·4939 grams.
Loss at 280°	0·1271 "
Required by theory of reaction 1, if Sb=120	0·1305 "
Total loss at red heat; that is, in both stages	0·2179 "
Required by theory of reactions 1 and 2	0·2174 "

It was evident from this determination that the order of the decomposition was precisely that indicated by our reactions, although the end of the first stage was not quite so sharply marked as the end of the second; and this would naturally be expected.

As the residues obtained on distilling chloride of antimony showed, when further heated, precisely the same order of phenomena which we have just described, and when heated to redness yielded the same crystals of oxide of antimony as before, it was plain that the residue left on evaporating the chloride at a temperature not exceeding 120° was chiefly at least SbOCl; but that this when heated more intensely was converted into

$Sb_4O_5Cl_2$ before the temperature reached 280°, and finally at a red heat was converted wholly into Sb_2O_3. We therefore endeavored to determine the amount of oxichloride in one of our preparations of chloride of antimony by distilling a weighed amount from a platinum nacelle at as low a temperature as possible in a current of dry carbonic acid, and heating the residue to a temperature of about 275°. We thus obtained the following results:—

No.	Wt. of $SbCl_3$.	Residue.	% of residue $Sb_4O_5Cl_2$.
1.	6·7286	0·0212	0·315
2.	4·5150	0·0151	0·334
3.	7·9320	0·0258	0·325

In order to yield 0·146 per cent of oxygen, which would reduce the per cent of chlorine in the preparation from 47·020 to 46·608, as in the scheme on page 116, there would be required 1·155 per cent of $Sb_4O_5Cl_2$.

Although the results of the above determinations accord within a few per cent of the quantity estimated, yet it was perfectly clear during the course of the experiments that they did not at all represent the total quantity of the oxichloride present in the preparation examined. Not only was the composition of the preparation not materially altered by the slow distillation, —a fact shown by the determinations marked *e* in the table on page 47, and by which we were misled at the outset,—but also the product from our distillation yielded when distilled again apparently as much residue as before. In a word, we found the same phenomena repeated in these distillations at a low temperature which had been so noticeable when the chloride was distilled at its boiling point, and which are so strikingly illustrated by the results given on page 115. It is possible, as before suggested, that the effects might arise from a small additional absorption of water at the successive transfers which the repeated distillations involved; or, in the later experiments, from the circumstance that the very extensive apparatus employed for drying the carbonic dioxide was not completely effectual. Still, now that our attention has been called to the danger, and we had taken unusual precautions on both these points, the explanations suggested did not seem to us sufficient; and we came to the conclusion that the oxichloride must distil over with the chloride of antimony to a certain limited extent, and that it was only an excess above this definite amount which was left behind as residue. Of course, SbOCl not only is not volatile, but is at once decomposed by heat; and we do not suppose that this compound by the tension of its own vapor is carried over in distillation. It is a very dilute solution, as it were, of SbOCl in $SbCl_3$ which thus distils; and the distillation of the oxichloride may resemble the carrying over of

boracic acid by the vapor of water, and similar phenomena, the result, as it is has always appeared to us, of a feeble kind of chemical union which has been usually designated by the term "molecular combination." Such a theory would account for the remarkable constancy which we have found in the chlorine determinations of the various preparations of antimonious chloride purified by distillation. But, on account of the very great difficulty of removing all possible disturbing causes, we found it impossible to obtain a rigid experimental demonstration of our theory without much more time and labor than we could then command. We hope to return to the subject hereafter. Meanwhile, however, it was evident that we could place no reliance whatever on the results just obtained. Nevertheless, the determinations were of value on account of the contrast between these results and those of a similar series of experiments on the residues from antimonious bromide which we collect in the following table:—

No.	Wt. of $SbBr_3$.	Residue chiefly $Sb_4O_5Br_2$.	% of residue.
1.	2·8342	0·0010	0·035
2.	2·0220	0·0006	0·030
3.	4·6730	0·0010	0·021

As will be seen, this residue is less than one-tenth of that obtained from the chloride, and is practically insignificant. Evidently, then, in the determination of the atomic weight of antimony more accurate results may be expected from the analysis of the bromide than from the analysis of either the chloride or the iodide of this element. The intermediate position of the bromide renders it, in a very remarkable way, the most stable of the three compounds. It absorbs moisture far less eagerly than the chloride, and it absorbs oxygen far less readily than the iodide, and is thus in great measure protected against each of these two sources of the same impurity.

We come finally to the new analyses of antimonious chloride we had undertaken. Fortunately, some of the old preparation that had been distilled so often had been preserved. It had been boiled for a long time since the last analyses were made, and kept in the same flask used for determining its boiling point, which had stood meanwhile tightly corked in a desiccator over sulphuric acid. The solid mass in the flask was easily broken up without exposure to the air by simply heating it to the melting point, and shaking it in the flask as soon as, beginning to melt, the mass had separated from the glass. Near its melting point, chloride of antimony becomes very friable, and is thus easily reduced to coarse powder, whence probably the old alchemistic name of butter of antimony. It is also worthy of notice that neither the bromide nor the iodide

acts in this way, as we found out in more than one instance to our cost.

Thus we were readily able to prepare our material for analysis, and, by a thorough mixing of the mass, to insure that the several samples taken had a uniform composition. In regard to the antimony determination, no further details are necessary. It was conducted, as described before, with every minute precaution which experience had suggested; and we give the full details, in order to show how completely we had been able to overcome the difficulties which it at first presented, and we feel confident that there is no process of wet analysis which is capable of giving more accurate results than this.

Details of Antimony Determination.

The antimonious chloride was first transferred to a very carefully dried weighing tube, and thence to the large flask in which it was dissolved. The transfer to the weighing tube was made in a dry atmosphere, and only required two or three seconds. It is evident, however, that a slight absorption of moisture at this point is not important; for, even if it increased the apparent weight of the assay by several milligrams, it would only reduce to a barely perceptible extent the percentages of all the constituents leaving the relative values wholly unchanged. It is only when, on boiling the chloride, after such an absorption, the chlorine is driven off, that the essential change of composition results.

Weight of tube and antimonious chloride	20·9609	grams.
" " after transfer to flask	16·3920	"
" chloride analyzed	4·5689	"

The weight of the tube and chloride while on the balance pan remained invariable for a sufficient length of time to give positive assurance of the constancy of the weights. The chloride was dissolved in a saturated solution of tartaric acid containing about 15 grams of the pure acid, and then diluted with carbonic acid and water and precipitated as before described. The precipitate, having been washed and collected as before, was dried in an air bath, at about 110°.

Weight of small filter	0·0434	grams.
" porcelain crucible	101·2132	"
	101·2566	"
" crucible and precipitate	104·6762	"
" red sulphide of antimony	3·4196	"

A portion of the dried precipitate dissolved in hydrochloric acid gave no residue. The rest was then transferred to a pla-

tinum nacelle, and heated, as has been described, in a current of dry carbonic dioxide gas. No sublimate was formed, and only a very slight empyreumatic odor could be perceived.

Weight of platinum nacelle	6·2493	grams.
" nacelle and dried precipitate	9·5273	"
" portion taken	3·2780	"
" nacelle and precipitate after heating to 285° for over half an hour	9·5234	"
Loss of weight of portion taken	0·0039	"
Corresponding loss for whole precipitate	0·0041	"
Weight of red sulphide as above	3·4196	"
" gray sulphide	3·4155	"

The carbonaceous residue left on dissolving this whole amount of gray sulphide in hydrochloric acid was barely perceptible. It was collected, however, as usual, on a weighed paper disk, and estimated.

Weight of small paper filter	0·0198	grams.
" same with residue	0·0212	"
" residue	0·0014	"
Calculated for whole precipitate	0·0015	"
Weight of gray sulphide as above	3·4155	"
Total weight of gray sulphide	3·4140	"
Corresponding weight of antimony assumed to be $\frac{5}{7}$ of the sulphide	2·4386	"
Per cent of antimony in the antimonious chloride under examination	53·374	"

It will be noticed that this result is practically identical with the mean of the previous determinations, which, as will be seen by reference to the table on page 48, was 53·401; and, by reviewing the facts stated in that connection, it will be perceived that this agreement is in itself alone a strong confirmation of the conclusion which we deduced from our first experiments on the synthesis of the gray sulphide of antimony,—that of the two values of the atomic weight of antimony in question, the lower is the more exact.

Coming next to the chlorine determinations, we noticed, for the first time, an effect which, under certain circumstances, may have an important influence on the accuracy of this well-known process, as employed in the analysis of chloride of antimony. In a precipitate of argentic chloride that had been deposited

from an unusually concentrated solution of antimonious chloride in tartaric acid, and had stood over night, our attention was called to some crystalline grains, which, on examination, proved to be a compound of tartaric acid, antimony and silver. We soon found that this product could be readily obtained by concentrating the filtrate from the precipitate of argentic chloride, and adding to it, while still warm, an excess of argentic nitrate. On cooling, the new crystals form in abundance. They have not yet been measured, but under the microscope they have the general aspect of right rhombic plates or prisms, with hemihedral modifications,—a general form which is so characteristic of the tartrates, and which we ourselves have previously studied in our crystallographic determinations of the tartrates of rubidium and cæsium.* We obtained for the amount of silver in the crystals, as a mean of three analyses, 26·30 per cent. The compound $Ag,SbO.H_2=O_4=(C_4H_2O_2).H_2O$ would require 26·34 per cent. The crystals may therefore be regarded as tartar emetic, in which the potassium has been replaced by silver; and they resemble the crystals of this well-known salt in general form. They are evidently the same substance obtained by Wallquist† by precipitating nitrate of silver with tartar emetic, and analyzed both by him and by Dumas and Piria. These chemists obtained respectively 27·31 and 28·05 per cent. of oxide of silver, which corresponds with the result given above as closely as could be expected; but they appear to have prepared the substance only in an amorphous condition. At least, in the description quoted, no mention is made of any crystalline form.

These crystals of argento-antimonious tartrate are apparently not acted upon in the least by cold water, and only slightly by boiling water; and finding this very insoluble material mixed with the precipitated chloride of silver, under the conditions stated, we were led to fear that it might be occluded to some extent by this precipitate, even when formed in much more dilute solutions of antimony and tartaric acid. The phenomenon was very similar to that we had already studied in the occlusion of the oxichloride by the sulphide of antimony; and there was reason to fear that, as in the previous case, an occlusion of this double tartrate might result, even when the substance would not otherwise be precipitated. How far such an action could have vitiated our previous results, it was, of course, now impossible to determine; but, as we previously stated, we had always taken great care not to add more than the slightest possible excess of argentic nitrate, and this was especially true in our more recent determinations. Now, however, we were

* Am. Jour. of Science and Arts, II, xxxvii, 70.

† Gmelin Handbook, Cavendish Edition, x, 326.

on our guard, and in the following determinations very great pains were taken to add just the requisite amount of the silver salt, and the argentic chloride was subsequently examined for traces of any such occlusion. But, excepting this close attention to well-known precautions, the determinations were made in the same way as before.

ANALYSIS OF ANTIMONIOUS CHLORIDE.

No.	Wt. of $SbCl_3$.	Wt. of AgCl.	% of Chlorine.
1.	2·2220	4·1682	46·407
2.	1·9458	3·6512	46·420
	Mean value		46·413

Bringing now the results together,—estimating the amount of oxygen by difference, as is usual in chemical analysis, and calculating what would be the composition of a preparation of antimonious chloride in which $\frac{2}{10}\frac{1}{0}\frac{3}{0}$ of a per cent. of oxygen had replaced an equivalent amount of chlorine, assuming, of course, Sb = 120 and Cl = 35·5,—we obtain the following very striking accordance:—

	Analysis.	Theory. Sb = 120, Cl = 35·5
Chlorine	46·413	46·418
Oxygen	·213	·213
Antimony	53·374	53·369
	100·000	100·000

The general conclusions, then, which we deduce as the results of this investigation, are—

First, that the value of the atomic weight of antimony found by Schneider in 1856—Sb=120 3—must be accurate within a few tenths of a unit, but that the most probable value of this constant, as deduced from our experiments, is Sb=120, when S=32.

Secondly, that the apparent disagreement with this result, presented by the partial analyses of antimonious chloride, is *probably* due to the constant presence of oxichloride in the preparations of this compound.

The investigation from the first has been a study of constant errors; and those who have followed us through the details will certainly allow that the opinions expressed at the beginning of this paper (on page 42) were not hastily conceived, even if they do not fully agree with our conclusions. In the attempts to correct or balance such errors, we have found at once the chief difficulties and interest of our work, and the secondary results thus reached seem to us the most important fruit of the whole investigation. Seeing, then, the sources of constant error we have discovered, and knowing that there are others

whose influence we have been able to trace, although we have not been able to define them as clearly as we could desire, it would be presumptuous in us to express too great confidence either in the correctness of our theories or even in the conclusiveness of our experimental results. Of this, however, we feel assured, that more trustworthy results cannot be expected from a repetition of the same processes until a more complete and accurate knowledge has been acquired of the substances employed. We have therefore proposed to ourselves a more thorough investigation of the haloid compounds of antimony, and the first results of this investigation we shall shortly publish. After the requisite data have been thus collected, we hope to return to the old problem with such definite knowledge of the relations involved as will enable us to obtain at once more sharp and decisive results than are now possible.

During the course of this investigation, we have been successively aided in the experimental work by Dr. F. A. Gooch, Mr. C. Richardson and Mr. W. H. Melville, at the time students in this laboratory; and without their assistance we could not have accomplished the great amount of labor it involved.

Harvard College Laboratory, June 12th, 1877.