ART. LXII.—*The Oxidation of Hydrochloric Acid Solutions of Antimony in the Atmosphere*; by JOSIAH P. COOKE. (Contributions from the Chemical Laboratory of Harvard College.)

IN our original paper on the Atomic Weight of Antimony—Proceedings of the American Academy of Arts and Sciences, vol. xiii, page 21—we made the following incidental observation in explanation of certain precautions which we found to be necessary in order to secure the precipitation of pure antimonious sulphide:

“The precautions here described may seem unnecessary to those who are not familiar with the fact that a solution of antimony in hydrochloric acid oxidizes with very great rapidity in the air,—fully as rapidly as the solution of a ferrous salt. A solution reduced as we have described, which has at first no action on the iodized starch paste, will strike the blue color after it has been exposed to the air for only a few minutes. This property of an acid solution of antimonious chloride is mentioned by Dexter, in the paper already referred to, but we were wholly surprised by the energy of the action. By means of it, antimony can be dissolved in hydrochloric acid without the aid of nitric acid, or of any other oxidizing agent save the air, if only a certain amount of antimonious chloride has once been formed. When, after exposure to the air, the solution is boiled over pulverized antimony, the solution is reduced, and a further portion of the metal enters into solution. After a second exposure, the same process can be repeated, and so on indefinitely. The process is very slow and tedious, but, in one experiment, we succeeded in bringing into solution in this way several grams of antimony.”

On the sole basis of this language we have been represented as asserting that such antimony solutions oxidize in the air as rapidly as a solution of *ferrous chloride*, and experiments on comparatively dilute solutions of antimonious oxide in hydrochloric acid have been adduced as proofs that our observation was incorrect.

As is evident from the context, the statement just quoted, although the result of a very extended experience, was not based on quantitative measurements. What we noticed was that the solutions *were very quickly acted on* by the oxygen of the atmosphere, and we freely admit that the expression here italicized is a more accurate description of our observation, than the words originally used as quoted above. But our meaning was not left in doubt, for we expressly say immediately after, that the process is very slow and tedious. In regard to the phenomenon in question, the effects are so obvi-

ous when once attention is called to them, that it is entirely unnecessary to confirm our previous observations except so far as to add the following quantitative determinations, which will serve to give an accurate idea of the extent of the action under the only conditions we have investigated, or in regard to which we have written.

In order to determine the amount of oxidation caused by the action of the atmosphere on a solution of antimony in hydrochloric acid, we reduced the oxidized solution by boiling the liquid over antimony bullets, and determined the loss in their weight. This method is fully described in our original paper, and is based not only on the reducing power of the metal, but also on the fact repeatedly observed, that after the reduction was complete, the smallest excess of the finely pulverized metal would not dissolve even after prolonged boiling, and in the presence of a large excess of acid, if only the solution was protected from oxidation.

We began our experiments by dissolving 1.0036 grams of pure antimony (a portion of the same used in our experiments on the synthesis of antimonious sulphide) in about 30 cubic centimeters of pure hydrochloric acid (sp. gr. = 1.175) adding 3 cubic centimeters of very dilute nitric acid (containing only about 5.4 per cent of HNO_3). After the solution was completed we added bullets made of pure antimony (the same that had been used in our previous experiments), and boiled the solution in an atmosphere of carbonic dioxide, using the same apparatus which we described in our previous paper (*loc. cit.*) After the reduction was ended, the solution was transferred to a flat-bottomed flask through a platinum tunnel, on which the bullets were retained, and after washing into the flask the last traces of the solution with as small an amount of hydrochloric acid as possible, the tunnel was removed, the bullets washed with water, and again weighed as at first on the platinum tunnel. In reducing the original solution 0.4100 of a gram of antimony were dissolved from the bullets. The solution now containing 1.4136 grams of antimony was next exposed to the air for different successive periods of time in a room having a varying temperature of from 15° to 30° , sometimes in the shade, and at other times on a window seat where the sun's direct rays fell on the flask during several hours of each clear day.

We give in the following table the weight of antimony dissolved from the bullets after each successive exposure to the air; the amounts in each case being determined with all the precautions described above and still more at length in our former paper:

Weight of Sb originally dissolved.....1.4136

1.	Dissolved from balls after 3 days' exposure,	0.0150
2.	do. after 5 days'	0.0295
3.	do. " 10 " May 17 to May 27,	0.0600
4.	do. " 23 " May 27 to June 19,	0.1340
5.	do. " 37 " June 19 to July 26,	0.2960
6.	do. " 120 " July 26 to Dec. 24,	0.4481 0.9826

During these experiments the volume of the solution was gradually increased by the hydrochloric acid used in washing as above described, so that at last the volume amounted to 100 cubic centimeters.

It will be noticed that the amount of oxidation increased with the time of exposure, and that so long as the amount was small it was as nearly proportional to the time as could be expected under the varying conditions. The increased activity shown by determination No. 5 appeared to be due to the intensely warm weather and bright sunshine during the period, and the last determination would seem to indicate that after the oxidation reached a certain limit the process went on more slowly as we should naturally expect, but, with the greatly varying conditions during this long period, no certain conclusion can be drawn in regard to the effect of any single cause.

The action we are discussing is entirely in harmony with the chemical relations of antimony. The most striking characteristic of this elementary substance is its tendency to form compounds of the radical antimonyl, SbO . The oxichlorides, the oxibromides and the oxi-iodides whose relations we have discussed so fully in our previous papers, are examples in point, and we have been continually surprised by the appearance of such compounds in reactions in the most unexpected ways. In this respect antimony closely resembles vanadium, and with this element antimony is more closely allied than with its familiar associate, arsenic. What the precise reaction is in the present case, we are not prepared to state. That it is not the simple conversion of a terchloride into a pentachloride we are convinced, and investigations are in progress which we hope will further elucidate the subject.

In this connection we may appropriately add that while the above determinations were in progress we repeated the experiment described on page 19 of our previous paper (*loc. cit.*). We treated in an open flask 5 grams of finely powdered pure metallic antimony with 50 cubic centimeters of strong and pure hydrochloric acid, to which we added only one cubic centimeter of the very dilute nitric acid (5.4 per cent) described above. The flask was placed in a warm protected place (30° C.) and shaken from time to time. Soon the acid became col-

ored reddish-yellow and the chemical action began. When it had apparently ceased, the contents of the flask were shaken together, and the solution became at once as colorless as water. But on standing in the air the color rapidly returned, spreading from the surface of the liquid downward. These phenomena were repeated again and again during four or five months, until the whole of the metal dissolved. According to the reaction usually assumed to take place under these circumstances, 5 grams of metal would have required 50 cubic centimeters of acid, so that the effect was obtained with only one-fiftieth of the amount required by this theory.