LVII.—*Action of Hydrogen Sulphide on Antimonic Acid Solutions.*

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(Communicated by Professor Bohuslav Brauner, Bohemian University, Prague.)

THE following is a condensed account of work done by Dr. Bošek under my direction in the University Laboratory at Prague.

From the analogy between arsenic and antimony, H. Rose (*Ann. Phys. Chem.*, 1859, **107**, 186) concludes that hydrogen sulphide throws down from a solution of arsenic acid or of antimonic acid a mixture of the respective trisulphides with sulphur, and that the pentasulphides of these elements can only exist in the form of sulphosalts. Bunsen (*Annalen*, 1878, **192**, 305), on the other hand, recommends the precipitation of antimony in the form of the pentasulphide for the quantitative estimation of this element. Willm (*Zeit. anal. Chem.*, 1891, **30**, 443) obtained results differing from those of Bunsen; he treated the freshly precipitated antimony trisulphide with caustic potash and chlorine, and, after repeated evaporation with hydrochloric acid, added tartaric acid and water, and precipitated the solution at 60—70° with hydrogen sulphide. Bunsen regarded the precipitate as pure antimony pentasulphide, but if prepared in this way or by decomposing Schlippe's salt with an acid, Willm found that it invariably lost part of its sulphur 3·5—13·8 per cent.). Thiele (*Annalen*, 1891, **263**, 71) was also unable to confirm Bunsen's results as regards the formation of pure antimony pentasulphide.

Brauner and Tomíček (*Trans.*, 1888, **53**, 145) found that on treating solutions of arsenic acid with hydrogen sulphide, either pure arsenic pentasulphide was obtained, in accordance with the statements of Bunsen, or, on varying the temperature, the rapidity of the gas current, the acidity of the liquid, &c., a mixture of the pentasulphide with the trisulphide and free sulphur was thrown down.

In the present paper, the results of a somewhat similar series of experiments are given on the action of hydrogen sulphide on antimonic acid under varying conditions.

Antimonic solutions were prepared either by dissolving the pure metal in a mixture of hydrochloric acid and potassium chlorate, or pure antimony trioxide was dissolved in caustic potash, and the solution treated with bromine or chlorine. In preliminary experiments, made with solutions prepared by the first method, it was soon found that it was most important to ascertain first whether the

tervalent antimony is completely oxidised to the quinquevalent state. This examination is the object of the first series of experiments.

I. *Action of Oxidising Agents on Antimonious Salts.*—This subject has been to some extent investigated by Kessler (*Ann. Phys. Chem.*, 1855, **95**, 204, 225; **113**, 134), whose method for the determination of the state of oxidation was used.* In the present experiments, the antimony was dissolved in hydrochloric acid at 15–20° or at 70–80°, varying quantities of potassium chlorate being added. The excess of chlorate was then destroyed by evaporation, and the solution was diluted with hydrochloric acid to a definite volume.

Experiment 1.—2·502 grams of antimony were treated with 30 c.c. of hydrochloric acid, and just enough potassium chlorate added to obtain complete solution of the metal. After treating as above described, and diluting to 100 c.c., 10 c.c. of the solution were mixed with 10 c.c. of hydrochloric acid and 80 c.c. of water, in order to satisfy the conditions prescribed by Kessler. Result: Unoxidised SbCl_3 = 28·08 per cent. and 28·05 per cent.

Experiment 2.—1·566 grams of metallic antimony were dissolved in 50 c.c. of hydrochloric acid and 1·75 grams of potassium chlorate at the ordinary temperature. Result: Unoxidised SbCl_3 = 17·68 per cent. and 17·65 per cent.

Experiment 3.—1·42 grams of antimony were dissolved at 60° in 50 c.c. of hydrochloric acid and 1·50 grams of potassium chlorate. Result: Unoxidised SbCl_3 = 12·35 per cent. and 12·33 per cent.

The amount of oxidation increases with increase in the quantity of potassium chlorate and increasing temperature, but complete oxidation could not be brought about in this way.

On evaporating in a vacuum over sulphuric acid the solutions obtained as above, beautifully crystalline, double salts were obtained. The first kind of crystals were colourless, transparent, of a hexagonal habit, but too unstable to be measured. Analysis shows that their formula is $2\text{KCl}, \text{SbCl}_3$. The other crystals were lemon-yellow, transparent, of a monoclinic habit, but too deliquescent to be measured. Their composition corresponds with the formula

	Sb.	Cl.	K.
Calculated for $3\text{KCl}, 2\text{SbCl}_4$	32·15	52·17	15·68
Found.....	31·29	52·38	15·38

* Kessler determines the amount of unoxidised, that is, trivalent antimony, by titrating a solution containing 20 per cent. hydrochloric acid with standard potassium dichromate in excess, destroying that excess with a standard solution of ferrous salt, and then again adding the dichromate solution carefully until a drop of the liquid no longer gives a blue coloration with potassium ferricyanide. (For details see also Brauner, *Trans.*, 1891, **59**, 62.)

Repeated attempts were made to obtain this substance again by mixing antimony trichloride, pentachloride, and potassium chloride in different proportions and evaporating the hydrochloric solution of these constituents in a vacuum, but the crystals could not be obtained again; it is uncertain, therefore, whether they are the double compound of the new antimony tetrachloride, SbCl_4 , or a mixture of double salts of the trichloride and pentachloride. On precipitating their solution with hydrogen sulphide, a peculiar reddish-pink sulphide was obtained, having the composition and the properties of *antimony tetrasulphide*, Sb_2S_4 , described in Experiment 32.

Some experiments were made in order to ascertain to what extent the oxidation of antimony can be effected by nitric acid.

Experiment 4.—To 0.222 gram of metallic antimony, 5 c.c. of fuming nitric acid were added drop by drop, and the crucible (covered) was then heated on a water bath for three hours. After evaporating to dryness, and finally removing the last traces of nitric acid by evaporation with hydrochloric acid, the residue was dissolved in hydrochloric acid and analysed, using Kessler's potassium dichromate method. Result: Unoxidised $\text{Sb}_2\text{O}_3 = 14.19$ per cent.

Experiment 5.—0.2355 gram metallic antimony was treated with 10 c.c. of fuming nitric acid as above. Result: Unoxidised $\text{Sb}_2\text{O}_3 = 4.87$ per cent.

Experiment 6.—0.2875 gram of antimony was treated with 15 c.c. of fuming nitric acid. Result: Unoxidised $\text{Sb}_2\text{O}_3 = 1.77$ per cent.

From this it will be seen that it is impossible to obtain pure antimonious acid, even when a large excess of fuming nitric acid is used.

The following series of experiments were made in order to ascertain the amount of oxidation produced by bromine water in alkaline antimonious solutions. Antimony trisulphide could not be used, as it dissolves only very incompletely in caustic potash. A solution of antimony in hydrochloric acid and potassium chlorate as obtained in Experiment 1, and containing a known percentage of the metal, was therefore chosen as the starting point. This was dissolved in caustic potash, always using the same quantity, and then varying quantities of bromine water were added. After heating for a definite time on the water bath, hydrochloric acid was added, and the decomposition of the hypobromite effected by evaporation, employing the precautions mentioned by Bunsen. The amount of unoxidised Sb_2O_3 was determined by Kessler's volumetric method.

Experiment 7.—0.1263 gram of antimony in alkaline solution was heated on a water bath with 20 c.c. of bromine water for two hours, &c., as above described. Result: Unoxidised $\text{Sb}_2\text{O}_3 = 12.67$ per cent.

Experiment 8.—Same quantities of antimony and bromine water as in Experiment 7, but the action was continued for four hours. Result: Unoxidised $\text{Sb}_2\text{O}_3 = 3.89$ per cent.

Experiment 9.—Same quantities of antimony and bromine water as in Experiments 7 and 8 were employed, but the mixture was heated for 10 hours. Result: Unoxidised $\text{Sb}_2\text{O}_3 = 1.51$ per cent.

Experiment 10.—Same quantities as in the foregoing experiments, but the heating was continued for 12 hours. Result: The oxidation was complete.

For the following experiments, solutions of pure antimony trioxide were treated as above.

Experiment 11.—0.204 gram of pure antimony trioxide, Sb_2O_3 , was dissolved in caustic potash, and heated with 30 c.c. of bromine water on a water bath for two hours, then decomposed with hydrochloric acid. Result: Unoxidised $\text{Sb}_2\text{O}_3 = 14.17$ per cent.

Experiment 12.—The same quantity of antimony solution as that used in Experiment 11 was heated with 30 c.c. of bromine water for 12 hours; the solution was then very gradually decomposed with hydrochloric acid. Result: Oxidation complete.

Experiment 13.—Same solution as in Experiment 7, 60 c.c. bromine water; time, one hour. Result: Unoxidised $\text{Sb}_2\text{O}_3 = 17.86$.

Experiment 14.—Same solution as in Experiment 11, 60 c.c. bromine water; time, one hour. Result: Unoxidised $\text{Sb}_2\text{O}_3 = 15.42$.

Experiment 15.—Same conditions as in Experiment 13, 50 c.c. bromine water; time, two hours. Result: Unoxidised $\text{Sb}_2\text{O}_3 = 12.46$. On comparing this experiment with Experiment 7, it is seen that the effect of the oxidising agent is almost entirely dependent on the time during which it acts. All the experiments show how difficult it is to bring about complete oxidation of antimony to the quinquevalent state. This important fact explains the discordant results obtained by the different authors who repeated Bunsen's experiments on the action of hydrogen sulphide on what were considered by them to be solutions of pure *antimonic* acid, but which, in reality, were mixtures of *antimonious* and *antimonic* compounds in varying proportions.

The action of these oxidising agents on *antimonious* compounds is at first rapid, gradually becoming much slower, and, on representing this graphically, a sharply-bent hyperbolic curve is obtained, having much the same character as the curve expressing the action of chromic action on hydrochloric solutions of tellurous acid (compare Brauner, Trans., 1891, 59, 66).

Action of Hydrogen Sulphide on Antimonic Solutions.

The following series of experiments were made with solutions of antimonic acid prepared as follows:—Antimony trioxide, pure and

especially free from arsenic, was dissolved in excess of caustic potash and a rapid current of chlorine passed into the solution for 12 hours; it was then several times evaporated down with concentrated hydrochloric acid until no more chlorine was given off. In order to see whether the oxidation of the antimony was complete, a portion of the solution was examined with standard potassium dichromate, and was found to be free from every trace of antimonious acid. The solution was then diluted to 1000 c.c., but it was found impossible to determine the amount of antimony present in an aliquot part, and to use the rest for further experiments, as an amorphous, white precipitate was slowly deposited. Therefore, as a starting point for the calculation of results, pure black antimony trisulphide was used, prepared by heating any of the precipitated sulphides in a current of carbonic dioxide at 210° , the product having the definite composition Sb_2S_3 (compare Paul, *Zeit. anal. Chem.*, 1892, **31**, 537). For precipitating, either gaseous hydrogen sulphide was used, or its solution made with water previously well-boiled and cooled; in order to avoid separation of sulphur, the excess of the gas was driven out by a rapid current of carbonic anhydride.

First Series of Experiments.

Experiment 16.—First of all, Bunsen's method was repeated in order to see whether really pure antimony pentasulphide is obtained in this way. 50 c.c. of the above solution were mixed with 14 grams of hydrochloric acid, the whole diluted to 100 c.c., and 200 c.c. of freshly prepared aqueous hydrogen sulphide added, stirring all the time; after removing the excess of the hydrogen sulphide, the precipitate was collected on a Gooch crucible filter, washed with water, then four times with alcohol, twice with a mixture of alcohol and carbon bisulphide, then four times with pure, redistilled carbon bisulphide, then four times with alcohol, after which it was dried at $105-107^{\circ}$. Result:

	A.	B.*
Weight of dried precipitate	0.2301	0.1889
Sb_2S_3 dried in CO_2 at 210°	0.1927	0.1589
Sb_2S_5 calculated from this	0.2294	0.1892
Difference	+0.0007	-0.0003

As the difference is within the limit of unavoidable experimental error, it is seen that by precipitating *completely oxidised* solutions of antimonious acid with aqueous hydrogen sulphide, *added at once*, and *at the ordinary temperature*, pure *antimony pentasulphide* is obtained. The pentasulphide is dark brown.

* As several weeks had elapsed between Experiments A and B, for the reasons above stated, 50 c.c. of the solution did not contain the same amount of antimony.

Experiment 17.—50 c.c. of the same solution as in Experiment 16 (*i.e.*, +14 grams HCl) were precipitated by passing a rapid current of gaseous hydrogen sulphide for half an hour, and the precipitate treated as above. Result:

Weight of dried precipitate	0.2287 gram.
„ Sb ₂ S ₃	0.1932 „
Composition of the original precipi- tate*	$\left\{ \begin{array}{l} \text{Sb}_2\text{S}_3 = 3.12 \\ \text{Sb}_2\text{S}_5 = 96.88 \end{array} \right.$
	100.00

Experiment 18.—50 c.c. of the same antimonie solution (*i.e.*, +14 grams HCl) were put into a beaker and 200 c.c. of hydrogen sulphide water added drop by drop from a burette with constant stirring. Even the first three drops produced an orange-coloured precipitate which rapidly increased. Result:

Weight of dried precipitate	0.1895 gram.
„ Sb ₂ S ₃	0.1602 „
Composition of precipitate.	$\left\{ \begin{array}{l} \text{Sb}_2\text{S}_3 = 3.32 \\ \text{Sb}_2\text{S}_5 = 96.68 \end{array} \right.$
	100.00

Conclusion.—When hydrogen sulphide acts on pure antimonie solutions for a longer time and therefore slowly, *not at once*, a partial reduction takes place.

In the following experiments, the influence of a larger quantity of hydrochloric acid present was studied.

Experiment 19.—50 c.c. of the same antimonie solution was acidified with 25 c.c. of hydrochloric acid, and aqueous hydrogen sulphide was added slowly from a burette. At first, free sulphur separated and produced a turbidity, and the first visible precipitate was obtained after the addition of 3 c.c. of hydrochloric acid; it took two and a half hours to add the 200 c.c. of aqueous H₂S. Result:

Weight of dried precipitate	0.1560 gram.
„ Sb ₂ S ₃	0.1325 „
Composition of precipitate.	$\left\{ \begin{array}{l} \text{Sb}_2\text{S}_3 = 5.39 \\ \text{Sb}_2\text{S}_5 = 94.61 \end{array} \right.$
	100.00

Experiment 20.—Experiment 19 was repeated, using 40 c.c. of hydrochloric acid, no separation of orange coloured precipitate from the

* From the above two data, the difference between the amount of Sb₂S₅ calculated from the Sb₂S₃ obtained, and the weight of the original precipitate and the molecular weight of Sb₂S₅, the amount of Sb₂S₃ and Sb₂S₅ is easily calculated.

turbid liquid took place until after the addition of 6 c.c. of hydrochloric acid. The very pale colour of the precipitate, and the strong turbidity of the alcoholic washings showed that much free sulphur was present. In fact, it was impossible to remove it completely, and as part of the sulphur present was in the form insoluble in carbon bisulphide, it must have been produced by oxidation of the hydrogen sulphide. Result :

Weight of dried precipitate	0.2090 gram.
„ Sb_2S_3	0.1710 „
Calculated weight of Sb_2S_5	0.2038 „
Difference	+ 0.0052 „

Owing to the strong reduction, 0.0052 gram of sulphur or 2.49 per cent. was found insoluble, over and above the theoretical quantity of pentasulphide, so that the percentage of Sb_2S_5 in the precipitate could not be calculated.

The present experiments show that the presence of an increased quantity of hydrochloric acid causes an increase in the reduction of the quinquevalent antimony compound, but owing to the separation of insoluble sulphur, as in Experiment 20, it is impossible to determine whether a precipitate formed in the presence of a large quantity of hydrochloric acid, is pure antimony pentasulphide, even if it *appeared* to have the same composition. From this point of view, some of the results obtained by Thiele (*Annalen*, 1891, **263**, 71) must be regarded with reserve. This author found that the quantity of antimony pentasulphide increased on increasing the amount of hydrochloric acid present from 2 to 10 per cent. It is possible that the maximum quantity of pentasulphide formed lies somewhere between 10 to 20 per cent. of hydrochloric acid, but it certainly diminishes above that limit.

Experiments at Higher Temperatures.

Experiment 21.—50 c.c. of the above antimonie solution were mixed with 14 c.c. of hydrochloric acid and diluted with water to 100 c.c. It was then heated to 70° by dipping the beaker in water of that temperature, and aqueous hydrogen sulphide was slowly added from a burette (the addition of 200 c.c. took $2\frac{1}{2}$ hours), which at first gave rise to a turbidity, and then produced an orange coloured precipitate. Result :

Weight of dried precipitate	0.1823 gram.
„ Sb_2S_3	0.1757 „
Composition of the precipitate....	$\left\{ \begin{array}{l} \text{Sb}_2\text{S}_3 = 77.17 \\ \text{Sb}_2\text{S}_5 = 22.83 \end{array} \right.$
	<hr/> 100.00

Experiment 22.—Experiment 21 was repeated at a temperature of 100°. The first drops of aqueous hydrogen sulphide produced, on the surface of the liquid, an orange coloured precipitate, which on stirring dissolved in the liquid and at the same time gave rise to a strong milky turbidity. Only after 15 c.c. of the reagent had been added (or after 9 minutes) was the first permanent, pale orange coloured precipitate obtained. It was treated very carefully to remove all sulphur. Result:

Weight of dried precipitate	0.1537 gram.
„ Sb ₂ S ₃	0.1503 „
Composition of the precipitate.	$\left\{ \begin{array}{l} \text{Sb}_2\text{S}_3 = 86.08 \\ \text{Sb}_2\text{S}_5 = 13.92 \end{array} \right.$
	<hr/> 100.00

Conclusion: With increase of temperature there is also an increase in the reduction and in the formation of antimony trisulphide.

It was now thought advisable to repeat Willm's experiments, namely, the action of hydrogen sulphide on antimonious solutions in the presence of tartaric acid, the reducing action of which Willm did not seem to suspect, any more than he did that of a high temperature.

Experiment 23.—50 c.c. of the above antimonious solution were diluted with 50 c.c. of water containing 1 gram of tartaric acid, heated to 70°, and precipitated by passing a rapid current of gaseous hydrogen sulphide. The liquid became milky at once, then, after 10 seconds, it acquired an orange colour, and after 25 seconds the first distinct precipitate was formed. After four hours (the passage of the gas was continued until the liquid became cold), the experiment was brought to an end. Result:

Weight of dried precipitate	0.0950 gram.
„ Sb ₂ S ₃	0.0898 „
Composition of the precipitate.	$\left\{ \begin{array}{l} \text{Sb}_2\text{S}_3 = 65.7 \\ \text{Sb}_2\text{S}_5 = 34.3 \end{array} \right.$
	<hr/> 100.0

The precipitate formed in this way, was considered by Willm to be pure, or approximately pure, antimony pentasulphide, whereas it consists of *two* parts of the trisulphide to *one* of the pentasulphide. The colour of such a mixture is always much lighter than that of the pure pentasulphide. Lastly, Willm states that such wet "pentasulphide" is *decomposed* into trisulphide and free sulphur, on washing with cold carbon bisulphide, a statement, the incorrectness of which is easily seen by comparing the Experiment 16 with Experiments 17—23, which show that the *pure* pentasulphide undergoes no such

decomposition (Experiment 16) whereas under the conditions obtaining in Experiments 17—23 pure pentasulphide cannot be obtained.

The contrary statements of Rammelsberg (*Ann. Chem. Phys.*, 1874, **52**, 193), and of Braun (Michaelis, *Anorg. Chem.* V, Bd. II, p. 598) when compared with those of Bunsen and the results described in the present paper are easily explained by the incomplete state of oxidation of the antimony in the solutions used by the two first mentioned investigators.

Second Series of Experiments.

The object of this series was to study the above cardinal reaction in the presence of some foreign substances. The solutions used were those of metallic antimony in hydrochloric acid and potassium chlorate, and in order to complete the oxidation the necessary amount of a solution of potassium dichromate was added. The amount of the last reagent was smaller in the preparations called *A* and larger in preparations *B*. The precipitate was in each experiment washed with alcohol and carbon bisulphide, &c., and after being dried, as previously described, was finally converted into black antimony trisulphide.

Experiment 24.—10 c.c. of solution were mixed with 50 c.c. of water, 5 c.c. of hydrochloric acid added, and then 13 c.c. of a solution containing 0.0324 gram of potassium dichromate to complete the oxidation. A rapid current of hydrogen sulphide was passed in for half an hour. Result :

Weight of dried precipitate	0.1990 gram.
„ Sb ₂ S ₃	0.1696 „
Composition of the precipitate.....	$\left\{ \begin{array}{l} \text{Sb}_2\text{S}_3 = 7.64 \\ \text{Sb}_2\text{S}_5 = 92.36 \end{array} \right.$
	<hr/> 100.00

Experiment 25.—Same quantities as in Experiment 24, except that the hydrogen sulphide was passed in a very slow current.

Composition of the precipitate.....	$\left\{ \begin{array}{l} \text{Sb}_2\text{S}_3 = 8.09 \\ \text{Sb}_2\text{S}_5 = 91.91 \end{array} \right.$
	<hr/> 100.00

Experiment 26.—10 c.c. of solution *B* were mixed with 50 c.c. of water, 5 c.c. of hydrochloric acid and 31 c.c. of a solution containing 0.0772 gram of potassium dichromate. It was precipitated with a rapid current of hydrogen sulphide. Result :

Weight of precipitate	0.2648 gram.
„ Sb ₂ S ₃	0.226 „
Composition of precipitate.....	$\left\{ \begin{array}{l} \text{Sb}_2\text{S}_3 = 8.37 \\ \text{Sb}_2\text{S}_5 = 91.63 \end{array} \right.$
	<hr/> 100.00

Experiment 27.—Same conditions as in Experiment 26, except that the gas was passed in in a slow current. Result :

Weight of precipitate	0.2833 gram.
„ Sb ₂ S ₃	0.2428 „
Composition of precipitate.....	$\left\{ \begin{array}{l} \text{Sb}_2\text{S}_3 = 10.58 \\ \text{Sb}_2\text{S}_5 = 89.42 \end{array} \right.$
	<hr/> 100.00

Experiment 28.—The above solution and 25 c.c. of hydrochloric acid were used ; the current of hydrogen sulphide was rapid.

Composition of precipitate.....	$\left\{ \begin{array}{l} \text{Sb}_2\text{S}_3 = 26.06 \\ \text{Sb}_2\text{S}_5 = 73.94 \end{array} \right.$
	<hr/> 100.00

Conclusions: The reduction of antimonie acid is larger in the presence of chromic chloride than in its absence and increases as the amount of that salt present increases ; it increases also with increase in the quantity of hydrochloric acid. The following experiments were made at a higher temperature.

Experiment 29.—10 c.c. of solution B, 15 c.c. of HCl, 31 c.c. of K₂Cr₂O₇, 50 c.c. of H₂O.

Slow current of H₂S was passed in at 50°. Result :

Weight of precipitate	0.1939 gram.
„ Sb ₂ S ₃	0.1885 „
Composition of the precipitate.....	$\left\{ \begin{array}{l} \text{Sb}_2\text{S}_3 = 82.58 \\ \text{Sb}_2\text{S}_5 = 17.42 \end{array} \right.$
	<hr/> 100.00

Experiment 30.—Same conditions as in Experiment 29, except that the hydrogen sulphide was passed into the solution heated at 70°. The solution became turbid, and an orange coloured precipitate was formed, which, after two hours, began to blacken, and became completely black when the gas was passed in at the said temperature for 10 hours. Result :

Weight of precipitate	0.1589 gram.
„ Sb ₂ S ₃	0.1559 „
Composition of the precipitate.....	$\left\{ \begin{array}{l} \text{Sb}_2\text{S}_3 = 88.21 \\ \text{Sb}_2\text{S}_5 = 11.79 \end{array} \right.$
	<hr/> 100.00

Experiment 31.—The precipitation took place at 100°. The orange coloured, amorphous precipitate formed was first converted into a distinctly crystalline, deep purple-red substance, with a violet tinge,

which, after three hours, began to slacken, and became quite black after 10 hours. Result:

Weight of precipitate	0.1621 gram.
„ Sb_2S_3	0.1608 „
Composition	$\left\{ \begin{array}{l} \text{Sb}_2\text{S}_3 = 94.89 \\ \text{Sb}_2\text{S}_5 = 5.11 \end{array} \right.$
	100.00

On filtering off the above precipitate, the perfectly clear filtrate deposited an orange coloured precipitate on standing; this was probably antimony pentasulphide, 0.0023 gram of the precipitate giving 0.0019 gram Sb_2S_3 (Sb_2S_5 requires 0.00193 gram Sb_2S_3).

Experiment 32.—The conditions were the same as in Experiment 31; and the formation of the intermediate pink crystalline sulphide was also observed. Result:

Weight of precipitate.....	0.1905 gram.
„ Sb_2S_3	0.1905 „
Composition of precipitate: Sb_2S_3 =	100.00 per cent.

Two problems presented themselves in the last series of experiments. The first was the appearance of the pink crystalline sulphide. Of the many attempts to isolate it, the following was not unsuccessful.

On passing the hydrogen sulphide at 50—55° into a solution which had required for its oxidation 31 c.c. of the above dichromate solution, a distinctly crystalline crimson-red or pink precipitate was obtained after eight hours. After removing all the free sulphur, it was dried at 106°, and gave 0.2070 gram of a substance which yielded 0.1886 gram of Sb_2S_3 (= 0.1347 Sb). Sulphur from the difference = 0.0723 gram.

The results agree perfectly with those required by the formula Sb_2S_4 .

	Calculated.		Found.
2Sb	240	65.2	65.1
4S	128	34.8	34.9
	368	100.0	100.0

In all the other experiments made, heterogeneous precipitates were obtained, which were either orange, brown, or partly black, according to the time during which the hydrogen sulphide had acted. Their approximate composition was

Sb_2S_3	85
Sb_2S_5	15
	100

The second problem was the reducing action of the chromic salts.

Experiment 33.—25 c.c. of antimonic solution *A* was mixed with a solution of 1.2413 grams of crystallised chromic chloride in 25 c.c. of water, and after dilution with 50 c.c. of water a slow current of hydrogen sulphide was passed in for three hours. Result:

Weight of dried precipitate	0.1496 gram.
„ Sb_2S_3	0.1222 „
This corresponds Sb_2S_3	0.1455 „
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Difference	+0.0041 or + 2.74 p. c.

In spite of careful washing, 2.74 per cent. of sulphur more were produced and left in the precipitate above the limit either of Sb_2S_5 or $\text{Sb}_2\text{S}_3 + \text{S}_2$, although the greater part of the precipitate consisted of trisulphide and sulphur, which, however, could be only partly removed.

Experiment 34.—The same solution as that used in Experiment 33 was precipitated with hydrogen sulphide and washed with water only, after which it was dried.

Weight of precipitate obtained	0.16025 gram.
„ precipitate in Exp. 33	0.1496 „
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Difference	0.01065 „

that is the amount of sulphur precipitated above the theoretical limit Sb_2S_5 , which was soluble in, and had been removed by, carbon bisulphide.

Conclusions.

From the experiments described in this paper, the following conclusions may be drawn.

1. The total conversion of antimonious into antimonic compounds by the action of oxidising agents is a very difficult matter, requiring a large quantity of the oxidising agent and a lengthened period of action.

Such reagents as fuming nitric acid, potassium chlorate in hydrochloric solution, and even bromine in alkaline solution, except when the last acts for very many hours, do not produce complete oxidation.

2. When an excess of hydrogen sulphide—in the form of aqueous solution—acts *at once* on antimonic solutions at the ordinary temperature, pure *antimony pentasulphide* is formed; this shows that if Bunsen's directions are strictly followed, exact quantitative results can be obtained.

3. On acting with hydrogen sulphide on antimonic solutions under otherwise similar conditions:

- a. The quantity of *antimony pentasulphide* increases :
 - α . The lower the temperature.
 - β . The more rapid the stream of hydrogen sulphide.
- b. The quantity of *antimony trisulphide* mixed with sulphur increases :
 - α . The higher the temperature.
 - β . The slower the action of hydrogen sulphide.

4. As regards the dependence of the quantity of both sulphides on the amount of hydrochloric acid present, it appears that the quantity of the *pentasulphide* formed increases with that of the acid up to a certain maximum, lying between 10 and 20 per cent. of acid, after which limit it rapidly diminishes, with increase in the amount of hydrochloric acid.

5. In the presence of chromic salts, acid antimonious solutions are reduced by hydrogen sulphide more easily and more completely than when they are treated without such an addition.

6. Pure antimony trisulphide is obtained from antimonious solutions only in the presence of chromic salts; a slow current of hydrogen sulphide must be passed during a longer time at a higher temperature, and then the trisulphide is deposited in the black modification.