

## PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XXVI.—*On Stibine.*

By FRANCIS JONES, F.R.S.E.

THE exact composition of stibine has never been ascertained, owing chiefly to the fact that the gas has not been obtained unmixed with hydrogen: nor does it appear likely that the gas can be prepared in the pure state, owing to its tendency to split up into antimony and hydrogen even at the ordinary temperature. Nevertheless it seemed to me not impossible to devise a method for the analysis of the gas even when mixed with hydrogen, and I have made a series of experiments in this direction, the results of which I propose to lay before the Society.

In the course of these experiments I had occasion to examine the properties of the gas and the different methods proposed for its preparation. These are:

(a.) By the action of acids on an alloy of zinc and antimony.

(b.) By the addition of a solution of antimony to a mixture of zinc and a dilute acid.

(c.) By the action of sodium-amalgam on a concentrated solution of antimony trichloride (Humpert, *Chem. Centr.*, 1865, 863).

The first and second methods yield a very impure gas (that is, a gas mixed with much hydrogen), and although the last gives a much purer product, it is unsuitable when large quantities are required. A more convenient method consists in allowing a strong solution of antimony in hydrochloric acid to drop on a considerable bulk of zinc either granulated or in powder. The gas may be purified by being passed through a very dilute solution of caustic soda, and then dried over calcium chloride and phosphoric anhydride. Prepared in this way the gas, although still mixed with a large excess of hydrogen, is so strong that it is frequently partially decomposed, and the sides of the generating flask (as in Humpert's process) become coated with a shining layer of antimony. It has a distinct nauseating odour, and an intensely disagreeable taste. The odour is not due, as has been stated, to the presence of traces of arsine, as it is quite noticeable when no trace of that gas is present. Stibine is soluble to a small extent in water; the solution tastes like the gas, is darkened by the addition of silver nitrate solution, from the formation of silver antimonide, and is precipitated by sulphuretted hydrogen in presence of hydrochloric acid. It appears to be poisonous,

as small fishes die in about two hours when placed in water through which the gas is passing; a fish on the point of death by the action of such water is revived by being placed in fresh water.

The solution of stibine in water decolorises solution of potassium permanganate, with separation of oxide of manganese; and when the gas is passed through solution of potassium permanganate, the colour likewise gradually disappears: in either case the filtered liquid contains antimony, but the precipitate is free from it. Arsine and phosphine act similarly on solution of potassium permanganate.

The degree of solubility of stibine in water was roughly estimated by passing equal quantities of the dry gas, and of the gas bubbled through a measured volume of water, into a series of bulb-tubes heated to redness, and previously weighed. From the amount of antimony\* deposited on the bulb-tubes in each case, the quantity of stibine taken up by the water was calculated. The following results were obtained:—

*Experiment A.*—Gain in bulbs. Stibine not passed  
through water ..... = 0.0910 gram.  
Gain in bulbs. Stibine passed through water .... = 0.0575 „

Antimony corresponding to stibine dissolved .... = 0.0335 „

Water used 1155 c.c. Temp. 10° C. Solubility = 5.32 c.c. per litre.

*Experiment B.*—Gain in bulbs. Stibine not passed  
through water ..... = 0.1674 gram.  
Gain in bulbs. Stibine passed through water .... = 0.1416 „

Antimony corresponding with stibine dissolved .. = 0.0258 „

Water used 1150 c.c. Temp. 10.5° C. Solubility = 4.12 c.c. per litre.

It has long been known that when stibine is passed through solution of soda or potash, the liquid is tinged yellowish-brown, then deep brown, and finally a black powder separates out. This brown solution is extremely oxidisable; simple shaking of an open flask containing it causes the colour to disappear almost instantly; it forms indeed a delicate test for the presence of oxygen. The solution rapidly decolorises solution of potassium permanganate. The composition of the black precipitate which separates out from such alkaline solutions has not been ascertained; it has been assumed to be an antimonide of sodium or potassium, but in careful examinations of different specimens I have uni-

\* A portion of the antimony in these experiments was invariably deposited in octohedral crystals. The crystalline form of some of them was discernible by the naked eye.

formly failed to detect the presence of either of these metals. The substance, however, was found to contain oxygen, and probably contains hydrogen also, and appears to be the same whether soda or potash is used for the preparation. The following analyses were made:—

|                       |              |                       |
|-----------------------|--------------|-----------------------|
| C contains. . . . .   | 87·48        | per cent. of antimony |
| D    "    . . . . .   | 84·64        | "       "             |
| E    "    . . . . .   | 86·70        | "       "             |
| Mean result . . . . . | <u>86·27</u> | "       "             |

The mean result agrees pretty closely with the formula,  $\text{SbOH}_3$ , which requires 86·53 per cent. of antimony. The substance is, however, unstable, and samples which have stood for some time contain a much larger proportion of antimony, as the following analyses show:—

|                                   |              |                       |
|-----------------------------------|--------------|-----------------------|
| F (from soda) contains . . . .    | 93·07        | per cent. of antimony |
| G    "       "       . . . .      | 92·90        | "       "             |
| H (from potash)   "       . . . . | 93·06        | "       "             |
| Mean result . . . . .             | <u>93·01</u> | "       "             |

The formula  $\text{Sb}_2\text{O}$  requires 93·84 per cent. of antimony, and this is possibly the substance obtained.

The composition of stibine has hitherto been only indirectly determined by the analysis of the compound formed by passing the gas through solution of silver nitrate. In this body the silver is supposed exactly to replace the hydrogen of stibine, and as Lassaigne (*Journal de Chemie Medicale*, xvii, 443) found the proportion of the atoms of silver to those of antimony as 3:1, it has been concluded that the formula of stibine is  $\text{SbH}_3$ . That little reliance can be placed on this method is evident from the fact that hydrogen alone is well known to decompose silver nitrate solution; and further, even if the formula of the silver compound be  $\text{SbAg}_3$ , it need not necessarily have been prepared from a body having the formula,  $\text{SbH}_3$ . In his paper on the action of hydrogen on silver nitrate (*Journal of the Chemical Society*, xxviii, 3), Russell mentions the occasional formation by that reaction of pure silver in the form of a network of fine filaments; I have frequently noticed the formation of such filaments of silver mixed with the black precipitate obtained by passing stibine through silver nitrate solution. It is evident, therefore, that the so-called silver antimonide is a mixture of that substance with metallic silver. The following determinations of the silver in this substance, all show a considerably higher proportion than is needed for the formula,  $\text{SbAg}_3$ , which requires 72·64 per cent. of silver:—

|   |          |       |           |           |                    |
|---|----------|-------|-----------|-----------|--------------------|
| I | contains | 79.74 | per cent. | of silver | } First specimen.  |
| J | "        | 79.46 | "         | "         |                    |
| K | "        | 77.17 | "         | "         | } Second specimen. |
| L | "        | 77.54 | "         | "         |                    |

There is unfortunately no method known for separating the free from the combined silver; I find, however, that by boiling the substance with a strong solution of common salt, a portion at least of the free silver is converted into chloride which is dissolved by the common salt. The silver antimonide after this treatment becomes lighter in colour and was found to contain 73.50 per cent. of silver. A small quantity of antimony also passed into solution by the action of the common salt. If the treatment be carried on too long, the quantity increases, and in one experiment in which the antimonide was repeatedly boiled with a strong solution of common salt, the residue contained 96.4 per cent. of silver.

#### *Eudiometric Analysis of Stibine.*

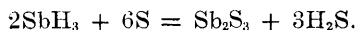
Although the impossibility of obtaining stibine unmixed with hydrogen prevents its analysis by the ordinary eudiometric method, I thought it would be interesting to ascertain, by a modification of that method, the relation between the amount of antimony deposited and the increase in volume of the gas after its decomposition by the electric spark. As the proportion of stibine to hydrogen is so small, it could not be expected that a measurable amount of increase could be obtained in an eudiometer of ordinary capacity, and it was therefore necessary to operate on larger quantities of the mixed gases. For this purpose the following method was adopted. A globe, having a capacity of more than 2 litres, provided with a long narrow neck, had fitted into it through a tubulus at the side, an india-rubber stopper, through which passed two platinum wires, to be connected with the induction coil. The neck of the flask was accurately graduated into cubic centimeters, and a millimeter scale was also engraved on it, so as to measure alterations in the level of the mercury in the trough and in the neck of the globe. The neck of the perfectly dry globe was dipped under the surface of the mercury contained in the trough, and the air it contained displaced by dry hydrogen: this again was displaced by dry stibine, and when the globe was judged to be full, the india-rubber tube by which the gas was admitted was clamped and withdrawn. The globe was then very gently heated, so as to expel a small quantity of gas, and thus raise the level of mercury in the tube to a convenient height for reading off. When the apparatus had become perfectly cold, the levels of the mercury in the tube and trough were read off by means of a telescope, and the temperature

and pressure noted. The platinum wires were then connected with an induction coil, and the spark was passed through the gas generally for about two hours. Very soon after the passage of the spark, fine filaments of antimony begin to deposit, especially in the neighbourhood of the platinum wires, which soon become coated with finely divided antimony. Occasionally these filaments, which vary in length from one to three inches, depend from the top and sides of the globe in a fine network. After the decomposition the globe was allowed to assume the temperature of the room, and similar readings were made as before. The first experiments were made simply to ascertain the amount of increase in volume; in the others the antimony deposited in the globe was washed out, oxidised with nitric acid, and determined as tetroxide. This latter operation was difficult to accomplish satisfactorily, owing to the small quantity of antimony to be determined, being spread over a large portion of the globe; moreover the amount of increase in volume produced by the decomposition was insignificant when compared with the total volume of the gas operated on. For these reasons the results obtained cannot be employed for determining the composition of the gas, but I give the details of the experiments, as they are not without interest in showing how small is the quantity of stibine present, even when prepared by a method which has been found to yield a mixture comparatively rich in that gas.

| Experiment. | Cor. vol.<br>before spark. | Cor. vol.<br>after spark. | Increase.   | Antimony.       |
|-------------|----------------------------|---------------------------|-------------|-----------------|
| M. . . .    | = 1098·44 c.c.             | 1099·42 c.c.              | = 0·98 c.c. | Not determined. |
| N. . . .    | = 1170·01 c.c.             | 1173·61 c.c.              | = 3·60 c.c. | „               |
| O. . . .    | = 1142·40 c.c.             | 1143·08 c.c.              | = 0·68 c.c. | „               |
| P. . . .    | = 2036·10 c.c.             | 2042·00 c.c.              | = 5·90 c.c. | „               |
| Q. . . .    | = 1756·93 c.c.             | 1763·56 c.c.              | = 6·63 c.c. | „               |
| R. . . .    | = 1717·57 c.c.             | 1722·73 c.c.              | = 5·16 c.c. | 0·0231 gram.    |
| S. . . .    | = 1725·70 c.c.             | 1731·08 c.c.              | = 5·38 c.c. | 0·0219 „        |
| T. . . .    | = 1713·78 c.c.             | 1718·21 c.c.              | = 4·43 c.c. | 0·0247 „        |
| U. . . .    | = 1826·08 c.c.             | 1829·22 c.c.              | = 3·14 c.c. | 0·0202 „        |
| V. . . .    | = 1841·63 c.c.             | 1842·82 c.c.              | = 1·19 c.c. | 0·0165 „        |

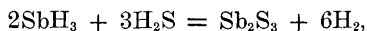
#### *Action of Stibine on Sulphur.*

In the course of these eudiometric experiments, I noticed that some of the india-rubber stoppers of the apparatus had become orange-coloured, and as this appeared due to the action of the gas on the sulphur of the stoppers, I proceeded to examine the action of sulphur on stibine. When stibine is passed over sulphur, it is decomposed, antimony sulphide is formed, and sulphuretted hydrogen liberated, according to the equation—



This reaction occurs at the ordinary temperature only in presence of light, the decomposition being slow in diffused daylight, but very rapid in sunshine. The same decomposition takes place slowly at the temperature of  $100^{\circ}\text{C}$ ., but becomes rapid when the sulphur is heated to higher temperatures; it is also brought about by the electric light, by that of burning magnesium wire, and even by the light of a good paraffin oil lamp.

It appeared to me that this reaction would afford a new means of ascertaining the composition of stibine, for the gas might be passed through a series of sulphur tubes (previously weighed), and the escaping sulphuretted hydrogen might be collected in an appropriate absorption apparatus. The amount of antimony could then be easily determined by adding to the gain in the weight of the sulphur tubes the amount of sulphur which had been withdrawn from them as sulphuretted hydrogen, and from the quantity of the latter gas the amount of hydrogen could be calculated. I accordingly fitted up an apparatus from which dry stibine was evolved, and allowed the gas to pass first through weighed U-tubes containing sulphur, then through a weighed calcium chloride tube (to absorb any moisture carried off from the sulphur), and then into a strong solution of copper acetate to absorb the sulphuretted hydrogen. The apparatus was placed close to a window, and kept in sunshine as much as possible. The sulphur very soon became orange-coloured, and so also did the empty portion of the U-tubes and the calcium chloride tube. This result was attributed to a secondary reaction taking place by the action of the stibine on the liberated sulphuretted hydrogen, according to the equation—



and this supposition was soon verified by exposing a mixture of these two gases contained in a flask to sunshine, decomposition then taking place, accompanied by deposition of antimony sulphide, which adhered firmly to the glass. This secondary reaction, by using up a portion of the sulphuretted hydrogen evolved, prevents the method being adopted without modification as a perfectly accurate one for determining the composition of stibine. To remove this source of error, the empty portions of the sulphur U-tubes were screened from the action of light by being covered with red cloth, and the calcium chloride tube and absorption apparatus were similarly protected. By this means the deposition of antimony sulphide was limited to the portions of tube containing sulphur, and the error was thereby greatly reduced. Several determinations were made with an apparatus arranged as follows: gas evolution flask; two wash-bottles containing dilute caustic soda; four U-tubes containing calcium chloride; two U-tubes con-

taining sulphur (weighed); two calcium chloride tubes (the first one weighed); wash-bottle, and three U-tubes containing solution of pure caustic soda. When the sulphur-tubes became deeply coloured they were removed, weighed, and replaced by fresh ones. The sulphuretted hydrogen was determined by passing chlorine through the soda-solution, and determining the amount of sulphuric acid formed, by precipitation with barium chloride, according to the method recommended by Rivot, Beudant, and Daguin (*Compt. rend.*, 37, 835).

The following results were obtained:—

| Experiment. | Gain in sulphur tubes. | Barium sulphate. | Hydrogen.   | H combined with 122 Sb. |
|-------------|------------------------|------------------|-------------|-------------------------|
| I. .... =   | 0·1308 gram.           | 0·2648           | = 0·00227 = | 2·11                    |
| II. .... =  | 0·0935 „               | 0·2043           | = 0·00175 = | 2·09                    |
| III. .... = | 0·3285 „               | 0·7421           | = 0·00637 = | 2·36                    |
| IV. .... =  | 0·1601 „               | 0·3693           | = 0·00316 = | 2·41                    |
| V. .... =   | 0·2335 „               | 0·4932           | = 0·00423 = | 2·21                    |

In experiments IV and V the quantity of sulphide adhering to the sulphur-tubes was estimated, and the amount deducted from the gain in weight of these tubes, while the amount of sulphuretted hydrogen to which it corresponded was added to that found in the caustic soda solution. When this correction is made the numbers become—

|            | Gain in sulphur tubes. | Hydrogen. | H combined with 122 parts antimony. |
|------------|------------------------|-----------|-------------------------------------|
| IV. .... = | 0·1365 gram.           | = 0·0037  | = 3·34                              |
| V. .... =  | 0·1982 „               | = 0·0051  | = 3·13                              |

From these experiments, and especially from the last, in which every precaution suggested by the previous preliminary experiments was taken, I conclude that the formula of stibine is correctly represented as  $\text{SbH}_3$ .

#### *Action of Stibine on Sulphur Compounds.*

The nature of the action of stibine on sulphur having been established by the preceding experiments, I proceeded to examine its action on some of the compounds of sulphur. When the gas is passed through carbon disulphide in presence of light, a black powder containing antimony and carbon separates out, and antimony sulphide is deposited in small quantity on the empty portions of the apparatus. This action takes place, however, very slowly, and I was not able to obtain sufficient substance for more than one analysis, which showed that the powder contained 78·68 per cent. of antimony. When stibine was passed through an alcoholic solution of mercaptan, a black powder,

similar in appearance to that obtained with carbon disulphide, separated out, but was not further examined.

Shiel has already shown (*Jahresbericht*, x, 211) that when stibine is passed through carbon disulphide, and then through a glowing porcelain tube, antimony sulphide is deposited, along with sulphur and a trace of carbon, while the escaping gas consists of hydrogen, sulphuretted hydrogen, some undecomposed carbon disulphide, and marsh-gas; while Humpert has shown that both stibine and arsine are decomposed by sulphuric acid (*Chem. Centr.*, 1865).

*Action of Arsine, Phosphine, and Ammonia on Sulphur.*

The behaviour of bodies analogous to stibine, with sulphur, is precisely similar. When *arsine* is passed over sulphur in presence of sunlight, decomposition takes place, and sulphide of arsenic is formed, while sulphuretted hydrogen is liberated. The latter gas is, however, decomposed by the excess of arsine, and a beautiful iridescent film of sulphide coats the tube. The decomposition is not effected nearly so readily as in the case of stibine.

*Phosphine* is also decomposed by sulphur, but much more slowly than either arsine or stibine, a yellowish-red phosphorus sulphide is formed, and sulphuretted hydrogen is evolved, although in small quantity (this may be due to the fact that phosphorus sulphide absorbs sulphuretted hydrogen).

*Ammonia gas* has been found to be absorbed by dry sulphur, and when heat is applied nitrogen and ammonium sulphide are produced; but the action does not appear to have been fully studied. In one experiment in which I exposed dry ammonia gas and sulphur to the action of sunlight for several weeks, I had indications of a reaction similar to that with stibine, although very much slower.

It is worthy of note that the facility of the decomposition of these bodies by sulphur increases with their molecular weights; and in this, as in so many other reactions, they show a uniform gradation of properties. Their tendency to react with sulphur extends also to their organic analogues, although the reaction is different. Hofmann (*Chemical Society's Journal*, vol. xiii, p. 289) long ago pointed out the remarkable facility with which triethylphosphine unites with sulphur to form the sulphide  $(C_2H_5)_3PS$ , while Buckton (*Chemical Society's Journal*, vol. xiii, p. 115) has shown a corresponding reaction in the case of triethylstibine. On the other hand, Hofmann found that triethylphosphine had no action, either on sulphuretted hydrogen or on mercaptan, but that it acted violently on carbon disulphide, producing the body  $(C_2H_5)_3P + CS_2$ ; he also ascertained that triethylarsine and triethylstibine are without action on carbon disul-



phide, even at the temperature of  $100^{\circ}$  C., and that phosphine is also unacted on, at all events at the ordinary temperature.

*The Reaction with Sulphur as a Test for Antimony.*

The reaction of stibine with sulphur affords an extremely delicate test for the presence of antimony. The most convenient apparatus to use for this purpose consists simply of a small flask (about 100 c.c. capacity) closed with a cork pierced with two holes, through one of which passes a funnel-tube, and through the other the bent-down limb of a small U-tube filled with calcium chloride. To the exit-tube of the latter is attached a narrow glass tube containing fragments of sulphur, which is kept in its place by plugs of cotton-wool. This tube hangs downwards, parallel to the limbs of the drying tube, so as to prevent the too rapid escape of the gas. In the flask are placed some pieces of pure zinc and some dilute hydrochloric acid, and the apparatus is placed in sunshine to ascertain the absence of antimony in the materials employed. Should no alteration occur in the colour of the sulphur, the liquid to be tested is then poured down the funnel-tube; if antimony be present the sulphur will soon become orange-coloured. The following experiments show the delicacy of the reaction:—

|               | Antimony<br>added to flask. | Appearance of sulphur.        |
|---------------|-----------------------------|-------------------------------|
| VI. . . . .   | 0.01 gram.                  | Deep orange colour.           |
| VII. . . . .  | 0.001 gram.                 | Distinct orange colour.       |
| VIII. . . . . | 0.0001 gram.                | Orange colour still distinct. |

In one or two cases so small an amount as 0.00007 gm. of antimony was detected with certainty. It must be borne in mind that this indicates a greater delicacy than is represented by the numbers, because by far the greater proportion of antimony remains in the flask with the zinc; indeed, according to the experiment of Rieckher (*Jahresbericht*, 1865, p. 255), the quantity of antimony deposited in the flask is to that evolved as gas in proportions varying from 92 : 8 to 96 : 4; so that, if these numbers be correct, quantities of antimony varying from 0.000006 gm. to 0.000003 gm. have been detected by the sulphur-test.

By means of this method I have detected antimony in several different samples of commercial zinc, but have not detected it in any sample of sulphuric acid which I have examined.

The delicacy of the test is not much diminished by the presence of arsenic. In one experiment, 0.0002 gm. antimony was detected in presence of fifty times as much arsenic, and in another experiment, 0.0001 gm. antimony was detected in presence of one hundred times as much arsenic.

Owing to the much greater facility with which stibine is decomposed, I attempted to separate it from arsine by this method; the separation was, however, incomplete. I have ascertained that with a sufficient surface of sulphur and in sufficiently bright sunshine, it is possible to absorb every trace of stibine by passing it through tubes filled with sulphur. On passing a mixture of arsine and stibine through several sulphur-tubes, all the antimony remains with the sulphur, and the greater proportion of the arsine passes through. If the escaping gas be passed through a solution of silver nitrate, the arsenic may of course be obtained. On exhausting sulphur so treated with solution of ammonium carbonate, the filtered liquid when neutralised with hydrochloric acid deposited only small quantities of arsenic trisulphide, so that the method may be used for the qualitative separation of antimony and arsenic, and is capable of detecting exceedingly small quantities of either metal.

When paper which has been coated with sulphur by being dipped in a solution of that substance in carbon disulphide, is surrounded with stibine and exposed to sunlight, it very quickly becomes uniformly orange-coloured, the time required being proportional to the strength of the gas and to the brightness of the light. I attempted to make this property the basis of a photometric process with fair success; the chief objection lies in the difficulty of obtaining and preserving the stibine of uniform strength. But for this difficulty the method would have the advantage over that commonly employed, that the papers obtained, as soon as withdrawn from the apparatus, would themselves form pictures, which by the intensity of their colour would indicate the power of the chemically active rays; moreover, so far as I have been able to observe, the colour of the marks so obtained is unaltered by exposure to air and light.

I need scarcely say that such paper as I have described, when connected with a suitable apparatus evolving stibine, may be used as a substitute for the ordinary sensitive silver papers used in photography, and copies of negatives may be got as in the ordinary process. The outline of such photographs is well marked, but they are wanting in delicacy of detail. The negatives used for this purpose soon become spoiled, owing to the deposition on them of a red film of antimony sulphide, which cannot easily be removed.

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