

LVIII.—*Action of Hydrogen Sulphide on Solutions of Antimonic, Arsenic, and Telluric Acids.*

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The object of the present research is a comparative study of a definite reaction which takes place with analogous compounds of certain elements, having regard to the position of these elements in Mendeléeff's periodic system.

The action of hydrogen sulphide on arsenic acid was studied by Brauner and Tomíček (Trans., 1888, **53**, 145), and shortly afterwards by Le Roy McKay.

An analogous work relating to antimonic acid has been done by Dr. Bošek, the results being given in the preceding paper. This work has naturally not exhausted the whole subject, but treating it from a somewhat empirical point of view has furnished material which may be taken as the basis of further experimenting and of a study of the mechanism of that reaction.

The following observation which I made many years ago formed the starting point of the work described in the preceding paper, and also of the present research.

A. *Action of Light on Antimony Pentasulphide.*

Antimony pentachloride was dissolved in hydrochloric acid and precipitated by the addition of 5 litres of an aqueous, saturated solution of hydrogen sulphide, subsequently passing a rapid current of gaseous hydrogen sulphide into the liquid; the orange coloured precipitate of antimony pentasulphide thus produced formed a layer several centimetres in thickness. The bottle containing the liquid and precipitate was placed in a window and exposed to full sunshine in the month of June, when it was observed that the precipitate became brown superficially, and after some time, black. It was then repeatedly shaken and exposed to the action of daylight or sunlight for about four years, when it was found to be so completely converted into a black, heavy crystalline powder, that only a few of the larger lumps showed traces of orange colour in the inside where the sunlight had no access. The volume of the original precipitate had diminished considerably.

This observation was made between the years 1887 and 1891, and the precipitate was analysed in order to see whether the black modification was trisulphide or pentasulphidene; a portion was dried, when it became grey, and on examination under the microscope it was seen that free sulphur was mixed with the black crystals.

Another part, after being well washed with water and alcohol, was repeatedly shaken with carbon bisulphide and again with alcohol, then dried and analysed.

0.4361 gave 0.3949  $\text{Sb}_2\text{O}_4$  = 0.3128 Sb. Sb = 28.51.

2.0412 „ 4.2384  $\text{BaSO}_4$  = 0.5821 S. S = 71.73.

|                    | Calculated for<br>$\text{Sb}_2\text{S}_3$ . | Found.       |
|--------------------|---------------------------------------------|--------------|
| Antimony . . . . . | 28.57                                       | 28.51        |
| Sulphur . . . . .  | 71.43                                       | 71.73        |
|                    | <hr/> 100.00                                | <hr/> 100.24 |

The black crystals, therefore, are pure antimony trisulphide, the original substance being a mixture of sulphur with black *antimony trisulphide* (black modification discovered by Mitchell, Abstr., 1893, ii, 473, by boiling the red modification with dilute hydrochloric acid in a current of carbon dioxide).

The formation of this black trisulphide from the orange pentasulphide is due to a slow *photochemical decomposition* by the rays of the sun, thus:  $(\text{Sb}_2\text{S}_5)_x + \text{Aq} = 2\text{S}_y + (\text{Sb}_2\text{S}_3)_z + \text{Aq}$ . It was impossible to observe whether the less molecularly complex red trisulphide was formed first. It should be added that the long time taken for the

completion of the above action was due to the fact that no less than 110 grams of antimony pentasulphide had been decomposed.

### B. *Action of Heat on Antimony Pentasulphide.*

It is well-known that on heating dry antimony pentasulphide in a current of an inert gas at  $210-220^{\circ}$ , it decomposes leaving the black trisulphide, whilst sulphur escapes. It seems of interest to ascertain whether, under favourable conditions, a similar decomposition might not occur at a lower temperature in the presence of water.

For this purpose 1000 c.c. of water was acidified with 100 c.c. hydrochloric acid and 50 c.c. of a solution of potassium antimoniate containing 0.412 gram of  $\text{Sb}_2\text{O}_3$  was poured in with continued stirring, so that a clear solution of antimonious acid was obtained. From this solution, pure antimony pentasulphide was precipitated by the addition of an excess of aqueous hydrogen sulphide. After pouring off one-half of the clear supernatant liquid, the other half containing the precipitate was treated with gaseous hydrogen sulphide. No change was observed to take place at the ordinary temperature. The mixture was then gradually heated to  $85^{\circ}$ , but after passing the gas for half a day the precipitate turned only slightly darker. It was then heated to  $95^{\circ}$  for half a day but no change took place.

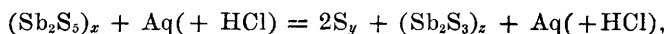
On raising the temperature, however, to  $97.5-99^{\circ}$ , the liquid began to boil very slightly, and the precipitate turned dark brown, and finally black; at the end of three hours it was completely converted into a black, crystalline substance, a mixture of black antimony trisulphide and free sulphur. After the latter had been removed as completely as possible by repeatedly washing it with alcohol and carbon bisulphide, the residue was dried at  $108^{\circ}$ . On heating at  $220^{\circ}$  in a current of carbon dioxide 0.4380 gram lost only 0.0054 gram of free sulphur, but it is very probable that the last was contained in it as an "insoluble" modification formed by decomposition of hydrogen sulphide at a high temperature and in the presence of acids.

The percentage composition of the precipitate is therefore:—

|                    | Found.      | Calculated for<br>$\text{Sb}_2\text{S}_3$ . |
|--------------------|-------------|---------------------------------------------|
| Antimony . . . . . | 70.5        | 71.4                                        |
| Sulphur . . . . .  | 29.5        | 28.6                                        |
|                    | <hr/> 100.0 | <hr/> 100.0                                 |

from which it is seen that the analysed precipitate consisted almost entirely of black antimony trisulphide.

At  $98^{\circ}$  the following decomposition therefore takes place:



and it is completely analogous to the decomposition by sunlight.

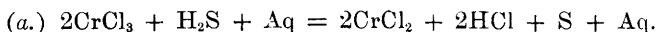
A similar formation of black antimony trisulphide was observed by Dr. Bošek in the presence of chromic chloride, and the question arose whether the last named substance does not promote the decomposition of the pentasulphide. The above experiment was repeated in the presence of chromic chloride, but I was surprised to find that, however vigorously the diluted or concentrated solution was boiled while a current of hydrogen sulphide was passed into it, no formation of black trisulphide took place.

### C. *Catalytic Action of Chromic Chloride Solutions.*

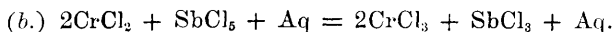
If, however, as has been shown in the foregoing paper, chromic chloride is added first to the antimonious acid solution, and hydrogen sulphide is then passed in, a much stronger reduction of quinquivalent antimony to trivalent is observed than in the absence of the chromic salt and at the same time hydrogen sulphide is oxidised, and sulphur, partly in the "insoluble" form, separates.

A "catalytic" action takes place which is so far of interest as it is generally assumed that a solution of chromic chloride is not reduced by the action of hydrogen sulphide. I find, however, on passing hydrogen sulphide into a hot green solution of chromic chloride, that its colour becomes first violet and then of a deep blue, and strongly dichroitic. On working with the purest preparation, I find that some sulphur is always separated, so that a *slight* reduction to chromous salt may have taken place, although not a trace of a chromous compound could be detected in the liquid. I think that the "catalytic" action of chromic chloride may be explained by the following hypothesis.

In the hot liquid, chromic chloride is reduced, to a very slight extent indeed, to chromous chloride, thus:—

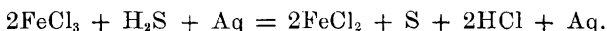


the chromous chloride reduces the antimonious to antimonious chloride;



after which the reaction (a) takes place again and so on.

This hypothesis would also account for the formation of "insoluble" sulphur, as, according to Selmi, it is formed when hydrogen sulphide acts on ferric chloride:



An analogous case was observed by Brauner and Tomíček on acting with hydrogen sulphide on a mixture of ferric chloride and arsenic acid.

D. *Analogy of Antimonic and Arsenic acids in their behaviour towards Hydrogen Sulphide.*

It is of some interest to compare the action of hydrogen sulphide on antimonie acid (Bošek) with that of hydrogen sulphide on arsenic acid (Brauner and Tomiček).

Arsenic and antimony are both members of the fifth group of Mendeléeff's system, the first belonging to the fifth series, the second to the seventh series. Antimony is therefore the next "atomic analogue" of arsenic.

During Bošek's work the question arose, What is the analogy and what the difference between the two elements when hydrogen sulphide acts on the aqueous acid solutions of their highest oxygen compounds?

Here a surprising analogy was observed, for both acids, under these circumstances, give either pure pentasulphide or a mixture of pentasulphide with the trisulphide and free sulphur, the following being the conditions.

*Antimonic Acid.*

- (1.) More  $Sb_2S_5$  is formed :
  - (a.) The lower the temperature.
  - (b.) The more rapid the current of  $H_2S$ .
  - (c.) The larger the quantity of  $HCl$  present (up to a certain limit).
- (2.) More  $Sb_2S_3$  (and sulphur) is formed :
  - (a.) The higher the temperature.
  - (b.) The less rapid the current of  $H_2S$ .
  - (c.) The greater the difference from the limit of 10—20 p. c.  $HCl$ , upwards or downwards.

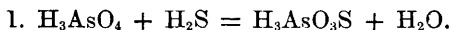
*Arsenic Acid.*

- (1.) More  $As_2S_5$  is formed :
  - (a.) The lower the temperature.
  - (b.) The more rapid the current of  $H_2S$ .
  - (c.) The larger the quantity of  $HCl$  present (up to what limit?).
- (2.) More  $As_2S_3$  is formed :
  - (a.) The higher the temperature.
  - (b.) The less rapid the current of  $H_2S$ .
  - (c.) The less  $HCl$  present (the limit upwards has not been investigated).

It is seen that the analogy between arsenic and antimonie acids, so far as the question was studied (we do not know whether a large excess of hydrochloric acid present may not promote the formation of arsenic trisulphide) is as complete as possible, and it is *à priori* probable that the mechanism of the action may be the same. At the conclusion of the paper on arsenic acid, quoted above, I said it was impossible to explain as yet why a *small* quantity of hydrogen sulphide causes a formation of the *trisulphide*, whereas an excess produces only the *pentasulphide*, so that the question remains an interesting problem of chemical dynamics.

In 1888, Le Roy W. McKay threw considerable light upon that subject (*Amer. Chem. J.*, 1888, 10, No. 6). He found that on adding

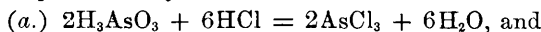
a *small* quantity of hydrogen sulphide to a cold dilute acidified solution of an arsenate, some free *sulphoxyarsenic acid*,  $\text{H}_3\text{AsO}_3\text{S}$ , was formed thus,



The *normal* reaction, which takes place between a solution of arsenic acid and a large excess of hydrogen sulphide is represented by the author thus,



whereas the formation of a mixture of arsenic trisulphide and sulphur, which takes place in the presence of a small quantity of hydrogen sulphide, especially at a higher temperature, is a secondary one, and is represented by him thus,



The question now arises: Is the great analogy shown, as regards the formation of either pentasulphide or a mixture of trisulphide and sulphur by both *arsenic* and *antimonic* solutions when treated with hydrogen sulphide, due to a strictly analogous chemical process?

Before trying to answer this question, we have to consider the well-known fact that when antimony is separated from arsenic by Bunsen's method (1878), in a solution containing both elements in the pentavalent state, the addition of hydrogen sulphide water causes the precipitation of antimony pentasulphide practically *at once*, whereas the arsenic acid remains practically completely in solution, while the excess of hydrogen sulphide is being driven out by a current of air.

After the liquid has been treated in the manner just described, Bunsen prescribes the addition of a few drops of chlorine water, undoubtedly with the object of oxidising some substance in solution. This substance may be either (*a*) arsenious acid, or (*b*) oxysulpharsenic acid, or (*c*) a small amount of hydrogen sulphide left in the liquid. As the question has never been discussed before, I may be allowed to say a few words about it.

Bunsen evidently intends to prevent the formation of any arsenic trisulphide by the subsequent action of the hydrogen sulphide.

Supposing (*c*) to be the aim, then, if a trace of hydrogen sulphide were left in the liquid—although this is highly improbable—it would certainly be destroyed.

As regards the oxidation of (*a*) arsenious acid, it is not very probable that it is formed during the process, and, if it were, that it would be entirely oxidised, as (*b*) the oxysulpharsenic acid undoubtedly present would also require chlorine for oxidation at the same time.

This last substance was unknown to Bunsen in 1877, and we have no available data regarding the amount or quantity in which it is formed during the process, but, if the few drops of chlorine water were supposed to destroy it entirely, its quantity must be very small.

In order to solve this question the following experiment was made.

*E. Action of Hydrogen Sulphide on Arsenic acid. Oxysulpharsenic acid.*

Five grams of arsenic trioxide was carefully and completely oxidised with nitric acid, the excess of the latter removed by evaporation, and the arsenic acid diluted with water to 1000 c.c.

Fifty c.c. containing 0.3589 gram of  $\text{H}_3\text{AsO}_4$  was acidified with 10 c.c. of hydrochloric acid, and 200 c.c. of a freshly-saturated aqueous solution of hydrogen sulphide was added. Not a trace of a precipitate or turbidity was obtained. After stirring for several minutes, exactly as is done when antimony is to be separated from arsenic by Bunsen's method, a rapid current of filtered air was passed through the liquid contained in a covered beaker under a bell-jar, by suction (this plan besides being automatic, answers the purpose much better than the use of a foot-blower) for one hour in order to expel every trace of hydrogen sulphide, although 10 minutes would have been sufficient.

On adding a few drops of bromine water, separation of sulphur took place, showing that all the sulphyarsenic acid had not been destroyed, as it was only after the addition of about 10 c.c. of a strong solution of bromine in potassium bromide (Gladding solution : 50 c.c. Br, 75 grams KBr, 500 c.c.  $\text{H}_2\text{O}$ ) that the sulphur present was entirely oxidised.

After removal of the excess of bromine, &c., the liquid yielded 0.2225 gram of barium sulphate, corresponding with 0.0306 gram of sulphur. This quantity represents 0.15074 gram of  $\text{H}_3\text{AsO}_3\text{S}$ , and as the arsenic acid present would have yielded 0.3991 gram of  $\text{H}_3\text{AsO}_3\text{S}$ , it is seen that 37.77 per cent. of the arsenic acid was converted into oxysulpharsenic acid. The sulphur found could only be from that compound, as 200 c.c. of the above hydrogen sulphide water when treated exactly in the same manner in a blank experiment (without any arsenic acid) gave no appreciable trace of barium sulphate.

The statement of McKay—"Sulphyarsenic is the end product, provided the amount of sulphuretted hydrogen which has acted on the arsenic acid is in comparison with the amount of arsenic acid in the dilute solution, *extremely small*"—requires alteration, for whereas the above quantity of arsenic acid requires 0.081 gram of sulphur for

complete conversion into oxysulpharsenic acid, as much as 0.4 gram of sulphur was present in the hydrogen sulphide used; that is, five times the quantity required, and one-thirteenth of that was really absorbed.

I may be allowed to remark here that experiments made in this laboratory have shown that arsenious acid may be separated from arsenic acid quantitatively exactly as proposed by Bunsen for antimony and arsenic.

It is also of historical interest, and certainly does not diminish Bunsen's claims, to find the germ of his classical method in Gmelin's *Handbuch*, 5th edition (1853), 2, 733.\*

#### F. Action of Hydrogen Sulphide on Antimonic acid.

Whereas arsenic acid is converted first into oxysulpharsenic acid, even when hydrogen sulphide is in excess, antimonic acid is precipitated by this reagent almost instantly, and here lies a great difference between the two acids.

Further, not only is oxysulpharsenic acid known, but also its stable salts (Bouquet and Cloëz, McKay); whereas oxysulphantimonic acid has never been obtained, and all attempts to prepare the oxysulphantimonates have hitherto proved futile. I shall return to this subject hereafter.

These facts are, *à priori*, against a complete analogy as regards the mechanism of the action between hydrogen sulphide and arsenic acid on the one hand and antimonic acid on the other.

Before attempting to study the last question experimentally, we have to consider the difference in solubility of the two acids in water. The sparing solubility of antimonic acid in water is a function of the atomic weight of antimony, that is, the oxy-compounds of antimony, as a higher member of the fifth natural group are of a less negative (or more positive) character than those of the lower members of that group. On account of its sparing solubility, it is somewhat difficult, in the case of antimonic acid, to establish the same conditions of experimenting as McKay has done with arsenic acid.

Again it is not possible to obtain a slightly acidified solution of

\* Antimony is tested for arsenic thus: "Its powder deflagrated (verpufft) with about one-fourth part of saltpetre and treated with water, gives a filtrate containing potassium arsenate and antimoniate. It gives, therefore, on supersaturation with hydrochloric acid and then rapid saturation with gaseous hydrogen sulphide, a yellowish-red precipitate of *antimony pentasulphide*; after rapidly filtering and keeping in a closed vessel, a yellow precipitate of *arsenic pentasulphide* is obtained after a time." Unfortunately the author of this long forgotten method is not given. (The italics are mine.—B. B.)



an antimoniate in the same way as it is with an arsenate, because in an aqueous solution of the relatively most soluble potassium antimoniate (the salt used in all subsequent experiments was that employed in qualitative analysis for the detection of sodium; its formula appears to me still somewhat doubtful), an insoluble precipitate of antimonious acid is produced on the addition of an acid. The only way in which a clear acid solution of antimonious acid could be obtained was by acidifying a large quantity of water with sulphuric or hydrochloric acid, and then pouring into it an aqueous solution of potassium antimoniate, stirring continuously. When too little mineral acid is used, a turbidity appears which cannot be easily removed.

For the following experiments, 15 grams of potassium antimoniate was dissolved in 1 litre of boiling water, and the cooled liquid filtered after a time. One hundred c.c. of the clear solution was found to contain a quantity of antimonious acid corresponding with 0.8236 gram of  $\text{Sb}_2\text{O}_3$ . This requires, for complete conversion into antimony pentasulphide, 220 c.c. of a freshly saturated solution of hydrogen sulphide containing about 0.2 gram of  $\text{H}_2\text{S}$  in 100 c.c.

Two thousand five hundred c.c. of water was strongly acidified with sulphuric acid and 100 c.c. of the above solution of potassium antimoniate was poured in, so that a clear solution was obtained. To this, 50 c.c. of hydrogen sulphide solution was added; an orange solution was produced, which, after some time, became opalescent. The hydrogen sulphide was so completely absorbed that its smell disappeared entirely after very short shaking of the closed flask. After a few hours, the opalescence changed to a turbidity, and at the end of 24 hours, a yellow precipitate separated of very nearly the same colour as the sulphides of arsenic.

In order to find whether it is not a compound corresponding to oxy-sulpharsenic acid,  $\text{Sb}_2\text{O}_3\text{S}_2$ , it was collected, repeatedly washed with a small quantity of water, and then successively with alcohol, with a mixture of alcohol and carbon bisulphide, with carbon bisulphide, and finally with alcohol. It was inferred by the turbidity of the filtrates that a large quantity of free sulphur was being washed out. After drying at  $100^\circ$ , it was analysed.

0.1164 gave 0.1035  $\text{Sb}_2\text{O}_3$ . Sb = 70.20 per cent.

0.1885 „ 0.0222  $\text{BaSO}_4$ . S = 1.62 „

From these data the calculated atomic proportion of sulphur to antimony is

$$\text{S} : \text{Sb} = 1 : 11.6,$$

which shows that the compound is not the expected oxysulphide, in fact, that it is not a definite compound at all. The large quantity of

free sulphur contained in it originally, that is sulphur from the hydrogen sulphide used for its precipitation, and amounting to 0.0941 gram, was almost entirely washed out by carbon bisulphide, and only 0.0049 gram of it was left in the precipitate as combined sulphur.

The following experiments were made with a hydrochloric solution of antimonious acid in order to avoid a possible admixture of sulphur from the sulphuric acid as used above.

Water, 2500 c.c., was acidified with 50 c.c. of hydrochloric acid, and 100 c.c. of the above antimoniate solution added; the clear solution was then mixed with 50 c.c. of hydrogen sulphide water. A deep orange solution was obtained, which in 15 minutes became opalescent and then turbid, and after 24 hours a yellow precipitate separated. This was collected, washed three times with a small quantity of water, then with alcohol and carbon bisulphide, dried, and analysed.

0.18125 gave 0.1679  $\text{Sb}_2\text{O}_3$ . Sb = 73.15 per cent.

0.1228 „ 0.0068  $\text{BaSO}_4$ . S = 0.76 „

0.1269 „ 0.0097  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O}$  = 7.64 „ (directly weighed after heating with anhydrous sodium carbonate in a current of air.)

Total 81.55 per cent. As the precipitate contains nothing except mere traces of chlorine and potassium which were too small to be determined, the missing 18.45 per cent. were taken as oxygen. I call this Precipitate A.

Precipitate B was obtained exactly in the same way, but its free sulphur was *not* removed by washing with carbon bisulphide.

0.2823 gave 0.2071  $\text{Sb}_2\text{O}_3$ . Sb = 57.92.

0.1761 „ 0.2144  $\text{BaSO}_4$ . S = 16.73.

0.1666 „ 0.0163  $\text{H}_2\text{O}$  by direct weighing.  $\text{H}_2\text{O}$  = 9.78.

Total 84.43 per cent. oxygen = 15.57 per cent.

In order to compare the composition of Precipitate A with that of B, the relation of combined sulphur to antimony was assumed to be the same in both precipitates, and, in addition to this, it was assumed that this sulphur was present in the form of antimony trisulphide. It does not alter the result much if it were present *partly* as pentasulphide. The percentage composition of the two precipitates is then—

|                               | A.           | B.           |
|-------------------------------|--------------|--------------|
| $\text{Sb}_2\text{S}_3$ ..... | 2.66         | 2.10         |
| Free S.....                   | —            | 16.13        |
| $\text{Sb}_2\text{O}_3$ ..... | 50.05        | 31.00        |
| $\text{Sb}_2\text{O}_3$ ..... | 39.65        | 40.99        |
| $\text{H}_2\text{O}$ .....    | 7.64         | 9.78         |
|                               | <hr/> 100.00 | <hr/> 100.00 |

It is seen from the above very carefully conducted analyses (1) that the original precipitate is not an oxysulphide; (2) that it contains a considerable quantity of free sulphur; (3) that it contains some antimonious acid, together with its reduction product—antimonious acid. The two acids could not have been held completely in solution during the action but must have been carried down along with the small quantity of the sulphide (or oxysulphide?) precipitated, for it is noteworthy that the same solution, without the addition of hydrogen sulphide, remains clear for days.

Two atomic proportions of sulphur should give one molecular proportion of antimony trioxide, or  $2S : Sb_2O_3 = 1 : 4.5$ , but the quantity of antimony trioxide found in the precipitate was really smaller, and so it was expected that some antimonious acid would be found in the original filtrates. This was proved to be the case by the following experiment.

The filtrate was precipitated with a large excess of aqueous sulphuretted hydrogen, the precipitate collected on a Gooch crucible, washed with carbon bisulphide, dried, and weighed. It was then converted into antimony trisulphide in a current of carbon dioxide at  $220^\circ$ , and weighed again. On multiplying the loss of weight (sulphur of the pentasulphide) by 6.2431, the quantity of pentasulphide is obtained. 0.4153 gram of the precipitate lost 0.0287 gram of sulphur. The percentage composition of the precipitate is

|                 |              |
|-----------------|--------------|
| $Sb_2S_3$ ..... | 56.86        |
| $Sb_2S_5$ ..... | 43.14        |
|                 | <hr/> 100.00 |

This shows that more than half of the antimony contained in the filtrate is found in the state of antimonious acid.

In order to more fully study the action of hydrogen sulphide on an excess of antimonious acid, the following two series of experiments were made.

*Series A.*—Ten c.c. of the above standard solution of potassium antimoniate requires 22 c.c. of hydrogen sulphide water for complete precipitation; so less than half this quantity, namely 10 c.c., was used.

The solution of antimonious acid was prepared in each case by acidifying 100 c.c. of water with  $n$  c.c. of sulphuric acid of 25 per cent., and then adding 10 c.c. of antimoniate solution, and afterwards 10 c.c. of sulphuretted hydrogen water with the following results.

(A 1.)  $n = 0$ ; solution perfectly clear and colourless; after some minutes, clear yellow, then an orange coloured turbidity. After 24 hours, only a trace of a precipitate is found at the bottom of the beaker. Hydrochloric acid gives a precipitate of antimony sulphide

and the same precipitate is obtained on adding a solution of ammonium chloride.

If much water is added to the original solution, it turns orange, but will keep perfectly clear for a long time; sometimes it will not give any precipitate even on adding an acid and a large excess of hydrogen sulphide. Such a liquid must be assumed to contain the solution of a colloidal form of antimony pentasulphide, probably free sulphantimonic acid.

(A 2.)  $n = 0.05$  c.c.; orange coloration at once; after one minute, a slight opalescence; no turbidity after one hour; at the end of 24 hours, a pale yellow turbidity.

(A 3.)  $n = 0.1$  c.c.; same as (A 2), the liquid becomes turbid, and after 24 hours a trace of a white precipitate separates from the orange solution.

(A 4.)  $n = 0.2$  c.c.; same as (A 3); no precipitate. After one hour, an orange precipitate begins to form; and, after 24 hours, another layer of a yellow precipitate is deposited upon the first. The supernatant liquid is colourless and slightly turbid.

(A 5.)  $n = 0.5$  c.c.; same as (A 4). Light orange precipitate after one hour, but the solution keeps clear the longest of the whole series. Later on, a paler precipitate separates, and the liquid becomes orange coloured and very turbid. After 24 hours the upper precipitate is pure yellow, and the supernatant liquid clear and colourless.

(A 6.)  $n = 1$  c.c.; orange turbidity at once; after shaking, a copious precipitate of the colour of antimony pentasulphide separates, and later on there is a precipitate of the colour of arsenic trisulphide. The supernatant liquid is colourless and slightly turbid, but from this, after 24 hours, a yellowish-white precipitate separates, and the liquid becomes perfectly clear.

(A 7.)  $n = 2$  c.c.; turbidity at once, and, after shaking, a copious orange precipitate; liquid almost clear.

(A 8.)  $n = 4$  c.c.; same as (A 7).

(A 9.)  $n = 8$  c.c.; same as (A 8).

(A 10.)  $n = 16$  c.c.; same as (A 9).

(A 11.)  $n = 32$  c.c.; same as (A 10); liquid clear.

*Series B.* The conditions were the same as in A except that only half the volume of  $H_2S$ -water, that is, 5 c.c. was added.

(B 1.)  $n = 0$ ; solution clear and colourless; after 24 hours, an orange opalescent turbidity, but no precipitate.

(B 2.)  $n = 0.05$  c.c.; pale yellow, clear solution, becoming opalescent; after one hour, a strong yellow opalescence; after 24 hours, a pale yellow turbidity, but no precipitate.

(B 3.)  $n = 0.1$  c.c.; clear yellow solution; after one hour, strong

white opalescence; after 24 hours, a pure white precipitate separated from the clear, colourless liquid. According to an analysis, the white precipitate contains free sulphur, together with antimonious and antimonie acids, but absolutely no sulphur is combined with antimony.

(B 4.)  $n = 0.2$  c.c., darker yellow solution, then opalescence. After one hour, strong, white opalescence; after 24 hours, a white precipitate. When more acid is present than in B 3 and B 4, some antimony will be separated as sulphide, and this increases with the quantity of free acid present.

(B 5.)  $n = 0.5$  c.c., clear yellow solution, which keeps transparent the longest of the whole series. After one hour, a strong, yellowish-white opalescence; after 24 hours, a nearly white precipitate with a slight, sulphur-yellow shade.

(B 6.)  $n = 1.0$  c.c., solution clear yellow, soon becomes turbid. After one hour, a precipitate of the colour of arsenic trisulphide, liquid same turbidity; after 24 hours, a yellow precipitate.

(B 7.)  $n = 2$  c.c., solution at once turbid. After 24 hours, a yellow precipitate with a white layer over it.

(B 8.)  $n = 4$  c.c.; same as B 7.

(B 9.)  $n = 8$  c.c.; same as B 8.

(B 10.)  $n = 16$  c.c.; same as B 9.

(B 11.)  $n = 32$  c.c., yellow turbidity. After one hour, pale orange flocks; liquid clear. No change after 24 hours.

After this, some of the precipitates obtained in a similar way were analysed.

To 2000 c.c. of water, 5 c.c. HCl, 100 c.c. of antimoniate solution, and 50 c.c. of  $H_2S$  water were added. A clear, yellow precipitate separated; this was washed with dilute hydrochloric acid and kept long in contact with an excess of hydrogen sulphide water, in order to convert free antimonious and antimonie acid into the sulphides. After washing with water, carbon bisulphide, &c., it was found to consist of

|                 |       |
|-----------------|-------|
| $Sb_2S_3$ ..... | 43.5  |
| $Sb_2S_5$ ..... | 56.5  |
|                 | <hr/> |
|                 | 100.0 |

The precipitate corresponding to (B 11) was prepared next by mixing 1000 c.c.  $H_2O$ , 320 c.c.  $H_2SO_4$ , 100 c.c. of antimoniate solution, and 50 c.c.  $H_2S$  water. An orange coloured precipitate separated *at once*.

On washing with carbon bisulphide, it evidently lost much free sulphur. It contained

|                               |        |
|-------------------------------|--------|
| $\text{Sb}_2\text{S}_5$ ..... | 59.95  |
| $\text{Sb}_2\text{S}_3$ ..... | 40.05  |
|                               | <hr/>  |
|                               | 100.00 |

G. *Hypothetical Potassium Oxsulphantimoniate.*

The precipitate corresponding to (B 1) was prepared by mixing 100 c.c. of antimoniate solution and 50 c.c. of hydrogen sulphide water. The solution soon became yellow, and then a pale orange opalescence was produced; on adding a saturated solution of ammonium chloride, an orange precipitate was formed. Half of the precipitate was analysed after filtration and washing with water only (A), the other half after washing with carbon bisulphide, when it was found to lose free sulphur (B); this precipitate is deep red.

A. 0.209 gram yielded 0.1698 gram  $\text{Sb}_2\text{S}_3$ . The precipitate contains therefore, for every 100 parts of  $\text{Sb}_2\text{S}_3$ , 23.09 parts of sulphur, free and combined.

B. 0.1564 gram yielded 0.1440 gram  $\text{Sb}_2\text{S}_3$ . The precipitate contains for every 100 parts of  $\text{Sb}_2\text{S}_3$ , 8.60 parts of combined sulphur.

From the above data the composition of the precipitate is calculated.

|                              |        |
|------------------------------|--------|
| Antimony trisulphide .....   | 44.56  |
| Antimony pentasulphide ..... | 43.67  |
| Free sulphur .....           | 11.77  |
|                              | <hr/>  |
|                              | 100.00 |

The composition of this precipitate, after the removal of free sulphur, corresponds very closely with that of antimony tetrasulphide.

In the experiments A 1 and B 1, and in that just described, salts of oxysulphantimonic acid ought to have been formed if they are capable of existence.\* In fact the solution originally obtained is colourless, and it is possible that it contains potassium oxysulphantimoniate,  $\text{K}_3\text{SbO}_4 + \text{H}_2\text{S} + \text{Aq} = \text{K}_3\text{SbO}_3\text{S} + \text{H}_2\text{O} + \text{Aq}$  (this equation being, of course, hypothetical†). This salt, however, is very unstable

\* Feit and Kubierschky (*Ber.*, 1888, 21, 1660) have made a series of experiments with the object of preparing oxygen derivatives of sulphantimonic acid (oxysulphantimonates, &c.). The results obtained were entirely negative, and the authors conclude from their experiments that derivatives of antimonious acid containing less than four atoms of oxygen replaced by sulphur are incapable of existence at the ordinary temperature. Their experiments are, however, not identical with those made above.

† Assuming that antimonious acid is a monobasic acid, the formulæ of it and of its derivatives in the above, and in the equations which occur later on, would become

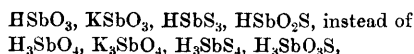
and decomposes very soon. The colourless liquid becomes yellow, then orange, and opalescent as described under  $A_1$  and  $B_1$ ; on adding ammonium chloride, a mixture of antimony pentasulphide and trisulphide with free sulphur is separated.

It should be added that this liquid containing, hypothetically, potassium oxysulphantimoniate, immediately after the hydrogen sulphide solution has been added, has the odour of that gas, and that, even if the quantity of the latter is insufficient to convert all the antimony into sulphide; silver sulphate also produces in it a black precipitate of silver sulphide. After several hours, however, when absorption of the hydrogen sulphide is complete, the liquid is yellow or orange, and decomposition has taken place. The solution with silver sulphate now gives a greyish-brown precipitate which after some time turns black.

A neutral solution of potassium antimoniate gives, with silver sulphate, a white precipitate; but a strongly acid solution, obtained by adding antimoniate solution to dilute sulphuric acid, is not precipitated by silver sulphate, although if silver sulphate or silver sulphantimoniate is precipitated from such a solution, the precipitate is invariably white. For this reason it was very difficult to repeat with such solutions McKay's reactions of oxysulpharsenates. When, however, an excess of hydrogen sulphide is added to a neutral solution of potassium antimoniate, decomposition occurs in a very short time with strong orange-coloured turbidity, followed by separation of an orange-coloured precipitate.

The above and this last mode of decomposition of a solution of the hypothetical oxysulphantimoniate of potassium is, however, perfectly analogous to the decomposition of potassium oxysulpharsenate during its formation. McKay has observed that on treating a hot solution of potassium arsenate with a rapid current of hydrogen sulphide, "a considerable amount of sulphide of arsenic" (trisulphide or pentasulphide? B. B.) "separates out." With potassium antimoniate, the same decomposition was observed by me to take place in the cold.

The study of this peculiar decomposition would be an interesting subject for further research. I am not quite satisfied with the results obtained, so as to be able to express the mode of decomposition of this hypothetical solution of potassium oxysulphantimoniate by means of an equation, and other work which I regard as more important does not allow me to devote more time to it.

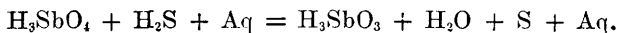


but this change is of no cardinal importance as regards the final conclusions arrived at.

### H. *Hypothetical Sulphantimonie and Oxy-sulphantimonie acids.*

It has been shown above that on acting on a solution of antimonie acid with an insufficient quantity of hydrogen sulphide, reduction to antimonious acid, accompanied by the separation of free sulphur, takes place after several hours.

Let us first consider the question whether this action could be explained by the "old reduction hypothesis."



This hypothesis is disproved by the following observations.

1. On adding to an acid solution of an antimoniate a quantity of hydrogen sulphide insufficient for complete precipitation of the antimony as pentasulphide, an orange, opalescent liquid is obtained. Hydrogen sulphide is so quickly and completely absorbed that the liquid smells of it only for a few seconds, and gives with silver nitrate or sulphate a black precipitate of silver sulphide. Immediately afterwards the atmosphere of the vessel is without action on lead paper, and silver sulphate produces only a light brown precipitate, which after many hours decomposes and becomes black. On account of the instability of the silver precipitate and of the solution, it was impossible to repeat with the latter McKay's reactions for oxysulpharsenic acid. It is, however, seen that hydrogen sulphide as such does not reduce antimonie acid, and that its sulphur is completely combined with antimony, most probably as sulphantimonie acid.

2. Very few experiments have been published from which we can judge as to whether antimonie acid is reduced easily or with difficulty by reducing agents. In order to answer this question, sulphurous acid in large excess was added to a solution of potassium antimoniate in sulphuric acid, and after it had been allowed to act for 24 hours, the excess was completely removed by a rapid current of air.

The liquid, from which some antimonious hydroxide had separated, was then strongly acidified with hydrochloric acid and precipitated with a large excess of aqueous hydrogen sulphide. The precipitate was collected, washed with carbon bisulphide, dried first at  $105^\circ$ , and then at  $220^\circ$  in carbon dioxide.

0.3125 gave 0.2999  $\text{Sb}_2\text{S}_3$ , so that the composition of the precipitate is

|                              |        |
|------------------------------|--------|
| Antimony trisulphide.....    | 74.83  |
| Antimony pentasulphide ..... | 25.17  |
|                              | <hr/>  |
|                              | 100.00 |

This experiment disproves the reduction hypothesis, for it shows that such a powerful reducing agent as sulphurous acid, even when

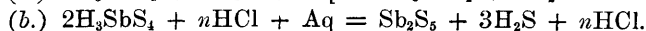
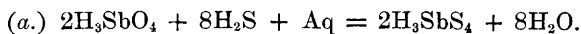


present in large excess and acting for a long time, is unable to reduce more than three-quarters of the antimonious acid present to antimonious acid, and thus a direct reduction by hydrogen sulphide becomes very improbable, especially as its sulphur combines directly with antimony.

Whatever the proportion between antimonious acid, free mineral acid, and hydrogen sulphide, it is always found that the sulphur of the hydrogen sulphide enters first into combination with antimony. The sulphide exists at first in a colloidal state in solution, so that the latter may be assumed to contain the hypothetical sulphantimonious acid  $\text{H}_3\text{SbS}_4$ .

Now we have the following alternatives.

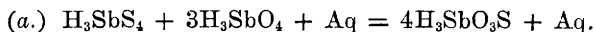
1.—When hydrogen sulphide is present in excess, together with a free mineral acid, the sulphantimonious acid produced at first is decomposed with formation of pure antimony pentasulphide.



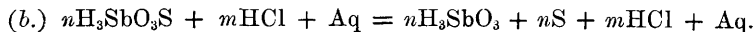
Here we have a cardinal difference between antimony and arsenic, for whereas arsenic acid is not precipitated by hydrogen sulphide until after the lapse of some time, a soluble form of antimony sulphide is produced at once in a solution of antimonious acid, as seen from the deep orange colour of the liquid. In this respect, antimonious acid resembles arsenious acid, or behaves very like the other more positive compounds of the metals of the hydrogen sulphide group.

2.—In the second alternative the antimonious acid is in excess over the quantity of hydrogen sulphide. On considering all the experiments contained in the present and the foregoing paper, the following explanation appears to me to be the most probable.

At first some sulphantimonious acid is also formed, but this, in contact with the excess of free antimonious acid present, combines to form oxysulphantimonious acid, thus



This must be a very unstable compound which, as soon as it is formed, decomposes into antimonious acid and free sulphur, thus



The deep orange colour of the liquid first formed, and corresponding to the state (a), disappears more or less completely on standing, and antimonious acid is formed, together with free sulphur, corresponding with the state (b).

This ideal case, corresponding with the decomposition of McKay's oxysulpharsenic acid at a higher temperature, was reached in the experiments (B 3) and (B 4), when a pure white precipitate, a mix-

ture of free sulphur with antimonious acid, alone separated. It depends also on the proportion of free acid present whether antimonious acid remains in solution or whether it is partly precipitated.

In the majority of cases described in this and the foregoing paper, the reaction 2 is accompanied by the reaction 1, for, as seen from the experiments (A 4—11) and (B 5—11), the presence of more free acid, *cæteris paribus*, causes the decomposition of a part of the sulphantimonic acid first formed, the antimony pentasulphide being precipitated instead of entering into unstable combination with antimonious acid. In addition to this, the action is complicated in so far as some antimony trisulphide is thrown down along with the pentasulphide, the trisulphide being formed most probably by the direct action of hydrogen sulphide on antimonious acid formed rapidly in the mode 2(b) when a large excess of free mineral acid is present. (See analysis corresponding with experiment B 11.)

That considerable time is required before the state of unstable equilibrium corresponding with the formation of oxysulphantimonic acid is reached is seen from Dr. Bošek's experiments 18 and 19 (this vol., p. 520), when the addition of hydrogen sulphide solution, even drop by drop, was too rapid to cause a reduction of more than 3—5 per cent. in two hours. It is unfortunate that the formation of *insoluble* sulphur, which takes place in the presence of a larger quantity of hydrochloric acid (experiment 20), complicates the phenomenon, as the presence of a large quantity of free mineral acid evidently promotes the rate of formation of oxysulphantimonic acid.

When working at a higher temperature, oxysulphantimonic acid is formed more rapidly, and reduction reaches 77 per cent. at 70° (experiment 21), whereas at 100° as much as 86 per cent. of antimony trisulphide is formed. Here the analogy to oxysulpharsenic acid is far more apparent, although, under the same conditions, the formation of arsenic trisulphide will undoubtedly reach a still higher percentage.

In all the reactions described, the more positive character of antimony as compared with arsenic appears distinctly, and this difference between the two elements corresponds exactly with their position in the periodic system, especially with that of antimony, as being a higher member of the fifth group than arsenic.

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Antimony forms a transition to the highest, most positive member of the same group, namely, bismuth, the pentavalent oxygen compound of which—a peroxide of the water type—oxidises hydrogen sulphide merely, and does not form a pentasulphide. The behaviour

of its trivalent compounds towards hydrogen sulphide brings it among the more positive metals of the mercury, lead, &c., group.

*I. Action of Hydrogen Sulphide on Telluric acid.*

The third analogous acid, the behaviour of which towards hydrogen sulphide has been investigated, is telluric acid. It is more negative than antimonious acid, owing to the position of tellurium in the same (seventh) series as antimony, and in its immediate neighbourhood in the sixth group. It forms a transition to periodic acid, which is so negative that it is not precipitated by hydrogen sulphide.

From the many experiments made by me with the object of studying telluric acid, and especially its behaviour towards hydrogen sulphide, only those are here of interest which show its analogy to or difference from arsenious and antimonious acids.

The behaviour of hydrogen sulphide towards telluric acid is closely analogous to its action on arsenious acid, not only in that its cold dilute aqueous solution, pure or acidified, is not at once precipitated by hydrogen sulphide, but also that a very long time elapses before precipitation takes place.

Brauner and Tomièk have shown that when an excess of hydrogen sulphide in the gaseous form acts at the ordinary temperature on a solution of arsenious acid, 97.83 to 99.37 per cent. is precipitated as sulphide after 24 hours, and 99.87 per cent. after 48 hours (Trans., 1888, 53, 147, 148, 151). McKay has proved that in a closely stoppered bottle complete precipitation takes place in two weeks.

Telluric acid treated in exactly the same way, that is, when an acid solution is put into a closely stoppered bottle with an excess of aqueous hydrogen sulphide, gives the first trace of a turbidity after the lapse of 24 hours, the first trace of a precipitate after two or three days, and even after being kept in the dark and cold for more than two months only a very small percentage is precipitated.

In order to find whether any sulphydrotelluric acid is formed in the cold, 0.2831 gram of crystallised telluric acid was dissolved in 50 c.c. of water, 10 c.c. of hydrochloric acid added, and then 200 c.c. of freshly prepared hydrogen sulphide solution. The liquid, from which nothing had been precipitated by hydrogen sulphide, was freed from the excess of this reagent by a current of air, after which it was oxidised in exactly the same manner as described under E. But whereas in the case of arsenious acid 37.77 per cent. of the latter was converted into oxysulpharsenic acid, not a trace of combined sulphur was found in the liquid in the case of telluric acid, proving that not a trace of sulphydrotelluric (oxysulphotelluric) acid was formed under the same conditions.

The excess of hydrogen sulphide was removed, after the lapse of

two days, from a mixture of 0.14 gram of telluric acid with 0.25 gram of sulphuric acid and 60 c.c. of hydrogen sulphide solution. The liquid was tested for sulphonyltelluric acid with silver sulphate solution, but not a trace of a precipitate was obtained in the acid or in the nearly neutralised solution.

In order to precipitate a solution of telluric acid completely by excess of hydrogen sulphide, the closed vessel containing the mixture must be heated in boiling water for six to eight hours at least, so difficult is it to precipitate telluric acid completely.

0.270 gram of pure crystallised telluric acid,  $\text{H}_6\text{TeO}_6$  (which is very difficult to prepare), after complete precipitation with hydrogen sulphide in a closed vessel and drying in a current of carbon dioxide for two hours at  $100^\circ$ , gave 0.2641 gram of a mixture of tellurium and sulphur corresponding with the atomic proportion of  $\text{Te} + \text{S}_3$  (the quantity calculated is 0.2632 gram). On heating at  $230^\circ$  in a current of carbon dioxide until the weight became constant, 0.1524 gram of tellurium was left (calculated 0.1501 gram).

0.270 gram of telluric acid, precipitated in the same way with hydrogen sulphide, gave 0.1534 gram after washing with carbon bisulphide and drying for two hours in a current of carbon dioxide at  $100^\circ$ . This residue is evidently a mixture of nearly pure tellurium with a trace of sulphur only, for on heating in carbon dioxide at  $230^\circ$  for three hours it yielded 0.1528 gram of residue.

These two experiments prove (1) that the precipitation is complete under the conditions described; (2) that the precipitate consists essentially of a mixture of tellurium and free sulphur in the atomic proportion  $\text{Te} + \text{S}_3$ ; (3) that from this mixture sulphur may be removed either by washing with carbon bisulphide or by heating at  $230^\circ$  in an inert gas. If any sulphur is *combined* with tellurium, its quantity is exceedingly small. These observations are of some interest with regard to the quantitative analysis and determination of telluric acid.

The following experiments were made in order to see whether any reduction takes place when hydrogen sulphide acts on telluric acid, the latter being in excess.

0.270 gram of telluric acid was dissolved in 150 c.c. of freshly boiled water and 30 c.c. of freshly prepared hydrogen sulphide solution was added, an amount sufficient to precipitate only one-half of the telluric acid present; the tightly closed flask containing the mixture was then heated in boiling water for two hours. As no mineral acid was added, a black liquid was obtained containing a solution of a colloidal modification of tellurium together with sulphur. In order to obtain a precipitate which could be filtered off, the flask was opened for a moment, and 1 c.c. of sulphuric acid of 25 per

cent. added, when it was perceived that the smell of hydrogen sulphide had not yet completely disappeared. The flask was then heated for two hours more at  $100^{\circ}$ , after which the hydrogen sulphide was found to be completely absorbed; the precipitate was collected in a Gooch crucible and dried for three hours at  $100-102^{\circ}$  in carbon dioxide; it weighed 0.1272 gram. It was then heated in the same gas for two hours at  $230^{\circ}$ , when it was found to weigh 0.0707 gram. The precipitate consisted, therefore, of 0.0707 gram of tellurium and 0.0565 gram of sulphur. According to the two foregoing experiments, the weight of the sulphur ought to have been 0.0517 gram, but, as calculated from the amount of hydrogen sulphide used, it should be 0.0565 gram—the weight really found. The excess of 0.0048 gram is therefore due to reduction.

It has hitherto been impossible to detect any trace of a sulphonyl-telluric acid in the filtrate.

The following experiment, analogous to Rose's experiment with arsenic acid, was made:—0.270 gram of telluric acid was dissolved in water, some sulphuric acid added, then hydrogen sulphide solution in excess, and the whole heated in an open beaker rapidly to boiling, until the excess of hydrogen sulphide was expelled. A small, very pale brown precipitate was formed which consisted of a very small quantity of tellurium together with a comparatively larger amount of sulphur. Here, evidently, reduction had taken place. This was proved by filtering off the precipitate and adding to the clear, colourless filtrate some hydrogen sulphide solution; a brown coloration was immediately produced, proving that the filtrate contained a small quantity of *tellurous* acid. No trace of sulphonyl-telluric acid could be found in the filtrate, so that, if it was formed, it must have been destroyed by boiling.

It should be noted that no sulphonyltellurates have hitherto been obtained, and that, therefore, judging from the analogy to antimony, sulphonyltelluric acid will be a very unstable substance. Its formation in the cold could not be observed, whereas if it were formed at a higher temperature it must have been immediately destroyed.

In order to test the "old reduction hypothesis," telluric acid was subjected to the action of sulphurous acid.

0.270 gram was dissolved in water and heated with 200 c.c. of aqueous sulphurous acid in a closed vessel for five hours; the precipitated tellurium was collected on a Gooch filter, washed and dried in carbon dioxide at  $100^{\circ}$ ; its weight was 0.0167 gram, or only about one-tenth of the total quantity (0.1526 gram) which is contained in the acid taken.

This proves how extremely difficult it is to reduce telluric acid even by such a powerful reducing agent as sulphurous acid, and,

for the same reasons as given in the analogous experiment made with antimonie acid, I conclude that the reduction hypothesis,  $\text{H}_2\text{TeO}_4 + \text{H}_2\text{S} + \text{Aq} = \text{H}_2\text{TeO}_3 + \text{S} + \text{H}_2\text{O} + \text{Aq}$ , is equally disproved.

### *Conclusions.*

Summarising the results of the experiments made with arsenic acid, antimonie acid, and telluric acid, it is seen that, as regards the property of not being immediately precipitated by hydrogen sulphide, telluric acid resembles arsenic acid, but it surpasses it in so far as it is acted on by that reagent with far greater difficulty. It is also far more difficult to reduce by sulphurous acid.

It differs from arsenic acid in so far as no sulphyxytelluric acid is formed in the cold.

It resembles antimonie acid in the arrangement of atoms corresponding with the formation of a sulphyxytelluric acid being very unstable, but it differs from it in that if the acid in question is formed at a high temperature it is immediately destroyed.

Tellurium differs, however, most essentially both from arsenic and from antimony, in the fact that tellurous acid as well as telluric acid when precipitated with hydrogen sulphide, give, as a final product of the action, precipitates consisting almost entirely of free tellurium and of free sulphur in the atomic proportions  $\text{Te} + \text{S}_2$  or  $\text{Te} + \text{S}_3$ . It is therefore impossible to investigate the question whether telluric acid when treated with hydrogen sulphide, under certain conditions, gives the bisulphide, and under other conditions the trisulphide, in the same way as this could be done with arsenic and antimony, for their sulphides are relatively stable.

The higher member of the sixth group, fifth series, selenic acid is not acted on by hydrogen sulphide at all in aqueous solution. The still higher member of the sixth group, third series, sulphuric acid is reduced by hydrogen sulphide directly:  $\text{H}_2\text{SO}_4 + \text{H}_2\text{S} = \text{SO}_2 + \text{S} + 2\text{H}_2\text{O}$  (in the absence of water).

The difference in behaviour of the acids in question is in complete accordance with what might be expected from the position of the corresponding elements in the periodic system.