CXCIV.—*The Solubility of Bismuth Trisulphide in Alkali Sulphides and of Bismuth Trioxide in Alkali Hydroxides.*

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STILLMAN (*J. Amer. Chem. Soc.*, 1896, **18**, 683) states that bismuth sulphide is soluble to a considerable extent in sodium sulphide, whilst Stone (*ibid.*, 1091), who confirmed this result, found that if the bismuth was first precipitated as sulphide from an acid solution, and then treated with alkali sulphide, little, if any, dissolved. Stillman precipitated a solution of bismuth nitrate with excess of sodium sulphide, warmed to a temperature near the boiling point for twenty minutes, filtered, and determined the bismuth in the filtrate. He gives, however, only one quantitative experiment, in which, moreover, the strength of the sodium sulphide employed is uncertain. Stone precipitated bismuth sulphide from a dilute acid solution of the chloride, filtered, and heated the precipitate with a large excess of potassium sulphide or of ammonium sulphide for half an hour. The undissolved sulphide was collected, redissolved, and the bismuth determined as the oxide. In both cases the bismuth trioxide found agreed with the amount of bismuth originally taken as chloride. Stone therefore concluded that bismuth sulphide, precipitated from acid solution, is not dissolved by subsequent treatment with alkali sulphides.

Neither author gives the method of preparation or the composition of the alkali sulphides employed. Since the term, "alkali sulphide solution," is applied in analytical chemistry to the solutions obtained by saturating the hydroxides with hydrogen sulphide to a greater or less extent, that is, to solutions of the alkali hydrosulphides or of the hydrosulphides and hydroxides in varying proportions, it is possible that such solutions were used by Stone,

instead of those containing the dissolved substance in the stoichiometric proportions represented by the formulæ Na_2S , K_2S , etc. This would explain the discrepancy between the results of Stone and those of the present investigation.

So far as the author is aware, no further work has been done on the solubility of bismuth sulphide in alkali sulphides. Owing to the important bearing of the subject on analytical chemistry, and to its interest from the theoretical point of view, the present investigation was undertaken in order to ascertain the nature of the reaction between bismuth sulphide and alkali sulphides, and the relation between solubility and concentration.

From the position of bismuth in the periodic system as the highest member of the fifth group, it might be expected that bismuth sulphide would, like the corresponding arsenic and antimony compounds, form complex anions with the sulphur ions of alkali sulphide solutions, although to a much smaller extent, on account of its greater electro-affinity compared with these elements (Abegg and Bodländer, *Zeitsch. anorg. Chem.*, 1899, **20**, 453; Abegg, *ibid.*, 1904, **39**, 330). Further, it is almost certain that the behaviour of bismuth sulphide towards solutions of sodium and potassium sulphides will be practically the same, owing to the similarity in constitution of the two solutions.

The bismuth sulphide used in the following solubility determinations was mainly "Kahlbaum's precipitated," which was freed from admixed sulphur by extraction with carbon disulphide and dried at 100—110°. It contained traces of oxychloride, which, however, in presence of the large excess of alkali sulphide used, have probably no effect on the solubility determination. In several experiments the bismuth sulphide used was prepared by precipitating a dilute solution of bismuth chloride, acidified with hydrochloric acid, with hydrogen sulphide, washing the precipitate, and drying at 100—110°. The sulphide so prepared gave the same solubility as Kahlbaum's. The sodium sulphide solutions were prepared by saturating a measured volume of standard sodium hydroxide, free from carbonate, with hydrogen sulphide in a graduated flask, expelling the excess of hydrogen sulphide by a current of hydrogen, adding a volume of sodium hydroxide equal to that originally used, and diluting to the mark with air-free distilled water. The potassium sulphide solutions were prepared similarly. The solubility in each strength of alkali sulphide was determined several times, and the alkali sulphide used in each determination was freshly prepared. This procedure eliminates, as far as possible, any error due to slight divergences in the composition of the solution from the theoretical, caused by the

impossibility of stopping the hydrogen current used to expel the excess of hydrogen sulphide at the exact point. These divergences will, however, always be small, since the concentration of undissociated hydrogen sulphide in alkali sulphide solutions, and hence the partial pressure of hydrogen sulphide over them is exceedingly minute (Knox, *Trans. Faraday Soc.*, 1908, **4**, 29). All operations were performed, as far as possible, in an atmosphere of hydrogen, so as to avoid oxidation of the solutions by atmospheric oxygen.

The solubility determinations were carried out as follows. The bismuth sulphide was shaken with the alkali sulphide solutions in a thermostat at 25° for about three days. In most cases experiments were also carried out in which the shaking was continued for a much longer period, in order to ensure that the equilibrium had been attained. In most cases, too, the equilibrium was attained from both sides. On the one hand, the sulphide solutions were shaken at 25° with bismuth sulphide until saturation occurred, and, on the other, the sulphide solutions were first saturated with bismuth sulphide at about 80°, and then shaken in the thermostat at 25° until equilibrium for this temperature was reached. The equilibrium attained under these different conditions was always the same. For the analyses, the bottles were hung in the thermostat until the solid had completely settled; 100 c.c. of the clear solution were then transferred to a beaker and carefully acidified with a slight excess of hydrochloric acid. This precipitated most of the bismuth sulphide, although the supernatant liquid remained brown, apparently owing to some of the sulphide remaining in colloidal solution, since the liquid cleared on standing. Hydrogen sulphide was passed in to complete the precipitation, and the precipitate was collected in a Gooch's crucible, washed with aqueous hydrogen sulphide, then with alcohol, and finally with carbon disulphide, and dried at 100—105°.

As will be seen from the tables, the agreement between the different determinations for a given concentration is not so good as is usual in a solubility determination, but this is probably accounted for by slight differences in the composition of the solutions, by differences in the size of the grains of the bismuth sulphide (Ostwald, *Zeitsch. physikal. Chem.*, 1900, **34**, 495), and by slight oxidation of the solutions.

The following table gives the solubility of dried precipitated

Concentration of sodium sulphide, mole/litre.	Number of determinations.	Bismuth sulphide dissolved: gram per 100 c.c. of solution, mean result.
0.5	5	0.0040 ± 0.0005
1.0	5	0.0238 ± 0.0016
1.5	3	0.1023 ± 0.0025

bismuth sulphide in sodium sulphide solutions. The solutions are greenish-yellow in colour.

In potassium sulphide solutions, the solubility for the same concentration is rather greater:

Concentration of potassium sulphide, mole/litre.	Number of determinations.	Bismuth sulphide dissolved : gram per 100 c.c. of solution, mean result.
0.5	4	0.0042 ± 0.0002
1.0	4	0.0337 ± 0.0017
1.25	5	0.0639 ± 0.0016

Since both freshly precipitated moist bismuth sulphide and dried precipitated bismuth sulphide dissolve in potassium sulphide solutions, it is difficult to explain the results obtained by Stone except on the assumption that he used potassium hydrosulphide instead of potassium sulphide solutions.

In the case of both sodium and potassium sulphides, the solubility increases rapidly with the concentration of the alkali sulphide, and is approximately proportional to the cube of the concentration.

The addition of alkali hydroxide to the alkali sulphide increases the solubility greatly. The following tables show the effect of sodium hydroxide and of potassium hydroxide on the solubility:

Solubility of Bismuth Sulphide in Sodium Sulphide with the addition of Sodium Hydroxide.

Concentration of sodium sulphide, mole/litre.	Concentration of sodium hydroxide, mole/litre.	Number of determinations.	Bismuth trisulphide dissolved : gram per 100 c.c. of solution, mean result.
0.5	1.0	7	0.0185 ± 0.0020
1.0	1.0	4	0.0838 ± 0.0022

Solubility of Bismuth Sulphide in Potassium Sulphide with the addition of Potassium Hydroxide.

Concentration of potassium sulphide, mole/litre.	Concentration of potassium hydroxide, mole/litre.	Number of determinations.	Bismuth sulphide dissolved : gram per 100 c.c. of solution, mean result.
0.5	1.0	4	0.0240 ± 0.0010
1.0	1.0	2	0.1230 ± 0.0014
1.25	1.25	1	0.2354

The solvent action of alkali hydrosulphides and hydroxides on precipitated bismuth sulphide was next investigated, since there was a possibility, judging from analogy to arsenic and antimony sulphides, that it might dissolve to a slight extent.

The hydrosulphide solutions were prepared by saturating the hydroxides with hydrogen sulphide, and expelling the excess of this gas by a current of hydrogen. Dried precipitated bismuth sulphide

was shaken with *N*- and 2*N*-sodium hydrosulphide and potassium hydrosulphide solutions for periods varying from twelve to twenty days. The solid was allowed to settle completely, and the clear, colourless, supernatant liquid withdrawn, faintly acidified with hydrochloric acid, and saturated with hydrogen sulphide. No trace of a precipitate or even of a brown coloration was obtained. On adding sodium hydroxide to the remaining sodium hydrosulphide solution, and again shaking for a few minutes, the solution assumed the greenish-yellow colour characteristic of solutions of bismuth sulphide in alkali sulphides. Bismuth sulphide is, therefore, insoluble in alkali hydrosulphides. This is also proved by the action of hydrogen sulphide on solutions of bismuth sulphide in alkali sulphides. On saturating such a solution with hydrogen sulphide, the bismuth sulphide is completely precipitated.

For the solubility experiments in alkali hydroxides, it was necessary that the bismuth sulphide used should contain traces neither of the oxide, which is slightly soluble in alkali hydroxides (see below), nor of the oxychloride, which reacts with alkali hydroxides to a certain extent giving the hydroxide BiO_2H (Herz and Muhs, *Zeitsch. anorg. Chem.*, 1904, **39**, 115). The first solubility determinations, made with dried precipitated bismuth sulphide, gave a solubility of the same order as that of bismuth oxide in alkali hydroxides. This was subsequently found to be due to slight oxidation of the sulphide during the drying, or to the presence of traces of oxychloride. It was found very difficult to prepare bismuth sulphide free from oxychloride by precipitation from a hydrochloric acid solution. Prolonged washing with aqueous hydrogen sulphide is necessary to remove the last traces of oxychloride. In order to avoid these sources of error, freshly precipitated, moist bismuth sulphide, which had been repeatedly washed with aqueous hydrogen sulphide and finally with air-free distilled water, was shaken with *N*- and 2*N*-sodium hydroxide for fifteen and thirteen days respectively. On acidifying the clear solution with hydrochloric acid and saturating with hydrogen sulphide, no trace of a precipitate or brown coloration was obtained. Bismuth sulphide is therefore insoluble in alkali hydroxides.

That the solutions of bismuth sulphide in alkali sulphides are not colloidal is proved by the following considerations. The same equilibrium is attained from both sides, and independently of the time of shaking. The solutions are quite stable; after months they still retain bismuth and their characteristic greenish-yellow colour, although they contain large quantities of electrolytes, which, as a rule, act as more or less rapid precipitants for colloids. The bismuth is not removed by filtering the solution through a very finely porous

cell. The fact that the solutions are prepared from dried precipitated bismuth sulphide is also against the probability of their being colloidal. Finally, the properties of the solutions do not agree with those of colloidal solutions of bismuth sulphide (Abegg's *Handbuch der anorg. Chem.*, III, 3, 662).

Since bismuth sulphide is insoluble both in alkali hydrosulphides and hydroxides, that is, does not form a complex anion with either SH' or OH' , its solubility in alkali sulphide solutions must be due to the formation of a complex anion with the sulphur ion, S'' , of these solutions. This view explains the increase in the ratio, bismuth sulphide dissolved/concentration of alkali sulphide, with increasing concentration of the alkali sulphide, and also the effect of the addition of alkali hydroxide in increasing the solubility of bismuth sulphide. The explanation is as follows. Sodium sulphide in aqueous solution is hydrolysed to a very large extent into sodium hydrosulphide and hydroxide (Küster and Heberlein, *Zeitsch. anorg. Chem.*, 1905, 43, 53; Knox, *loc. cit.*) according to the equation:

or, writing the ionic equation:

and, since it is the salt of a weak acid and a strong base, the hydrolysis must increase with dilution. The relative concentration of the S'' -ions must, therefore, diminish with dilution, and, since the solubility of bismuth sulphide depends on the S'' -ion concentration, the ratio of bismuth sulphide dissolved to sodium sulphide will also diminish with dilution. From the hydrolysis equation, it is also evident that the addition of alkali hydroxide, by increasing the concentration of OH' -ions, will diminish the degree of hydrolysis, thus increasing the concentration of the S'' -ion, and hence the solubility of bismuth sulphide in the alkali sulphide. The same considerations apply also in the case of potassium sulphide. The existence of the solid compounds KBiS_2 , NaBiS_2 (Schneider, *Pogg. Ann.*, 1869, 136, 460; Milbauer, *Zeitsch. anorg. Chem.*, 1905, 42, 433), and $\text{Bi}_2\text{S}_3 \cdot 4\text{K}_2\text{S} \cdot 4\text{H}_2\text{O}$ (Ditte, *Compt. rend.*, 1895, 120, 186) also confirms the view that the solubility is due to complex formation with the S'' -ion.

Bismuth sulphide, therefore, forms, like the corresponding arsenic and antimony compounds, complex anions with the S'' -ion, but not to an appreciable extent with SH' - or OH' -ions. From the solubility determinations alone, however, it is not possible to arrive at the formula of the complex.

The importance of this reaction in analytical chemistry has

already been emphasised by Stillman (*loc. cit.*). In the separation of the copper sub-group from the arsenic sub-group by means of alkali sulphides, the quantitative determination of bismuth would be vitiated, and small quantities of bismuth might easily be missed altogether.

The action of sodium disulphide and of ammonium sulphide solutions on bismuth sulphide was also studied, in view of their importance analytically in the separation of the copper and arsenic sub-groups.

The sodium disulphide solutions were prepared by dissolving the requisite quantity of sulphur (crystallised from carbon disulphide) in sodium sulphide solutions. In the solubility determinations, dried precipitated bismuth sulphide was shaken with the sodium disulphide solution until equilibrium was established. A definite volume of the clear solution was then withdrawn, and acidified with hydrochloric acid. The bismuth sulphide was precipitated along with the excess of sulphur. Hydrogen sulphide was passed in until the supernatant liquid became clear, when the precipitate was collected in a Gooch's crucible, washed with aqueous hydrogen sulphide, then with alcohol, and finally with carbon disulphide, dried, and weighed. The washing with carbon disulphide was repeated until the weight was constant. As the mean of four determinations, in which the times of shaking were varied greatly, 100 c.c. of *N*-sodium disulphide solution were found to dissolve 0.0090 ± 0.0010 gram of bismuth sulphide. This is only about a third of the solubility in the corresponding strength of the monosulphide. This result confirms the view that the solubility of bismuth sulphide in alkali sulphides is due to the formation of a complex anion with the S'' -ion, since in polysulphide solutions a large proportion of the S'' -ions are used up in forming the complexes S_2'' , S_3'' , etc., with the dissolved sulphur, and are, therefore, not available for complex-formation with bismuth sulphide. In solutions of the higher polysulphides, the solubility would be still less than in the disulphide.

The ammonium sulphide solution was prepared in the same way as the sodium sulphide, except that the hydrogen sulphide used to saturate the ammonia solution was washed by ammonia of the same strength, and the expulsion of the excess of hydrogen sulphide by a current of hydrogen was omitted. In *2N*-ammonium sulphide, which had been shaken with dried precipitated bismuth sulphide for ten days, no trace of dissolved bismuth sulphide was found. The exceedingly small concentration of S'' -ions in ammonium sulphide solutions (Knox, *loc. cit.*) explains the insolubility of bismuth sulphide.

Solubility of Bismuth Oxide in Sodium Hydroxide Solutions.

The bismuth oxide was prepared either by igniting the basic nitrate to low redness, or by precipitating the basic nitrate from a solution of the normal nitrate by diluting with water, digesting the precipitate on the water-bath repeatedly, first with water and then with sodium hydroxide solutions, washing until free from alkali, drying, and igniting. Both preparations gave the same solubility. The sodium hydroxide solutions used were free from carbonate.

The time of shaking required for the establishment of equilibrium was much longer than in the case of the sulphide solutions. As a rule, two to three weeks were allowed. The solubility determinations were carried out in the same way as for the sulphide. The clear saturated solutions were slightly acidified with hydrochloric acid, and the bismuth precipitated as sulphide. The results are contained in the following table:

Concentration of sodium hydroxide, mole/litre.	Number of determinations.	Bismuth oxide dissolved : gram per 100 c.c. of solution, mean result.
1·0	7	0·0013 ± 0·0002
2·0	6	0·0026 ± 0·0002
3·0	5	0·0049 ± 0·0005

The solutions were colourless, and showed no opalescence.

The solubility is nearly proportional to the concentration of the sodium hydroxide. A few experiments with potassium hydroxide showed that the solubility was much the same as in sodium hydroxide. The same arguments against the colloidal nature of the solutions hold as in the case of the sulphide solutions. Bismuth trioxide, therefore, behaves towards strong bases as the anhydride of a weak acid, but, in agreement with its more electropositive character, to a much less extent than the corresponding oxides of arsenic and antimony.

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