

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY
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MERCUROUS SULPHIDE.

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Received May 25, 1903.

IN the paper "On the Reactions between Mercury and Concentrated Sulphuric Acid,"¹ by F. W. Miller and the writer, two statements were made, which, while true for the conditions given, require modification in the light of knowledge recently gained. "The reaction is by no means like that of copper"² (p. 874) and "No sulphide was produced, nor any free sulphur" (p. 876). By great variations of one of the factors, time, sulphide was obtained. The experiment was continued through a period of five years and one week. Ten grams of pure mercury³ were covered with 50 grams of chemically pure sulphuric acid (99.65 per cent.) in a well-ground, glass-stoppered bottle of about 100 cc. capacity and allowed to remain at the temperature of the laboratory (never over 30° C.) for the period mentioned. While the bottle was never subjected to the direct rays of the sun, no attempt was made to shield it from the light.

When the bottle was opened, there was a strong outward pressure, and noticeable quantities of sulphur dioxide escaped. This corroborates the statements put forward in our second paper⁴ in controversion of the criticism of Pitman.⁵ Morley⁶ and Berthelot⁷ have also shown, independently, that mercury and sulphuric acid of maximum concentration react at ordinary temperatures with the evolution of sulphur dioxide.

The point of especial interest in the experiment lay in the simultaneous formation of a sulphide of mercury, which showed that the mercury resembles copper in this reaction more than was thought. Upon the bright metal there separated flakes, which resembled plates, of mercurous sulphide. The acid was decanted, a large volume of water added and quickly decanted. This was

¹ This Journal, 19, Nov., 1897.

² *Ibid.*, 17, Nov., 1895, and 18, Nov., 1896.

³ *Loc. cit.*

⁴ This Journal, 20, 515.

⁵ *Ibid.*, 20, 100.

⁶ *Loc. cit.*

⁷ *Chem. News*, 76, 325; *Compt. rend.*, 125, 20.

done several times. The bottle was inclined and revolved so that most of the sulphide was caused to cling to the sides of the vessel, the metallic mercury poured out and the sulphide thrown upon a filter and washed with alcohol (95 per cent.) until the wash-water was no longer acid. The brownish black plates (about 0.2 gram) were dried at 110° C. and analyzed by Mr. R. O. E. Davis of this laboratory.

Amount taken.	Sulphur found. Per cent.	Mercury found. Per cent.	Calculated for Hg ₂ S.
0.0866	8.23	7.41
0.0707	...	91.94	92.59
Total	...	100.17	100.00

The quantity remaining was too small to examine for the presence of free sulphur, although from the analysis it appears that 0.82 per cent. of free sulphur was present. As no quantitative determination of the sulphur dioxide, mercury sulphates produced, and so forth, were made, it is impossible to indicate the course of the reaction by an equation.

Authoritative works (Richter, Dammer, etc.) state that mercurous sulphide is not definitely known. Berzelius¹ said the black precipitate produced by hydrogen sulphide with mercurous salts was mercurous sulphide, but Barfoed² has shown that it is a mixture of mercuric sulphide and mercury. Antony and Sestini³ state that hydrogen monosulphide acting upon mercurous salts below 0° C. give mercurous sulphide, which above that temperature decomposes into mercuric sulphide and mercury.

Mercurous sulphide heated in a closed tube turns white (doubtless due to oxidation), becomes slightly yellow, then melts to a dark orange-brown liquid, which changes to a white solid on cooling, as does mercurous sulphate.

¹ *Archiv. d. Apothekervereins im nördl. Deutschland, von Brandes*, 18, 292.

² *J. prakt. Chem.*, 93, 230.

³ *Gazz. chim. Ital.*, 24, I, 193.