Stannous chloride found. Gram.	Stannous chloride theory. Gram.
0.3544	0.3523
0.4893	0.4903

Several attempts were made to separate stannous and stannic sulphides by this procedure. The results were unsatisfactory. In order to drive out the stannic salt completely it is necessary to heat the mixture, and this caused a partial volatilization of the stannous chloride, so that quantitative results could not be obtained.

Comparatively few metallic sulphides have been studied in the direction indicated in the preceding lines, so that it is probable a wider application of the method will disclose interesting behaviors, and that probably new separations can be brought about in this way. The action of the vapors of haloid acids has also been tried on natural sulphides with a fair degree of success.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 20.]

TUNGSTEN HEXABROMIDE.

BY HERBERT A. SCHAFFER AND EDGAR F. SMITH.

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THE most recent work upon tungsten bromides is that of Roscoe,[1] who endeavored to prepare a hexabromide, but obtained instead a penta derivative from which the dibromide was subsequently made. By reference to the literature bearing upon this subject it will be noticed that bromine, diluted with carbon dioxide, was made to act upon tungsten metal exposed to a red heat. Experimental evidence is at hand that tungsten at high temperatures deoxidizes carbon dioxide, thus allowing ample opportunity for the production of oxybromides, which, in spite of the greatest care, are sure to appear in larger or smaller amount. The thought also suggested itself that possibly the "red heat" at which the action was allowed to occur might have been detrimental and have indeed prevented the formation of the hexabromide.

Hence, we determined to operate in an atmosphere of nitro-

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[1] *Ann. Chem.* (Liebig), 162, 362.

gen and to apply a very gentle heat to the vessel containing the tungsten. In this connection it may be mentioned that the nitrogen was conducted through a series of vessels charged with chromous acetate, sulphuric acid, caustic potash, and phosphorus pentoxide, respectively. It then entered an empty vessel into which dry bromine was dropped from a tap-funnel, and after passing through a tall tower, filled with calcium chloride, entered a combustion tube resting in a Bunsen furnace. The anterior portion of the combustion tube was contracted at intervals, forming a series of bulbs, and at its extremity was connected with an empty Woulff bottle, followed by a calcium chloride tower, and finally a receiver filled with soda lime and broken glass. A steady current of nitrogen was conducted through this system for a period of three days. On the fourth day bromine was introduced. The tungsten contained in the combustion tube was heated very gently. In a short time brown vapors appeared. These condensed to a liquid beyond the boat and eventually passed into blue-black crystalline masses that separated from the walls of the tube, when perfectly cold, with a crackling sound. Very little heat was required to melt them and they could with care be resublimed in distinct, blue-black needles. The latter was collected in one of the bulbs (No. 2) previously mentioned. Other products were observed and isolated. All were analyzed. Bulb No. 1—that nearest the tungsten metal—contained a black, velvety compound, which upon analysis showed the presence of tungsten dibromide. Bulb No. 2 contained 0.2103 gram of the blue-black crystals, which yielded 0.0577 gram of tungsten, or 27.43 per cent., and 0.1543 gram of bromine, or 73.53 per cent. The theoretical requirements of tungsten hexabromide are 27.72 per cent. tungsten and 72.28 per cent. bromine. The bromine percentage found is high. This may be due to traces of bromine that had not been driven out from the crystalline deposit, or to adherent silver tungstate, as some tungstic acid remained in the solution from which the silver bromide was precipitated.

A fresh portion of the blue-black crystals was prepared as before and analyzed. The bromine determination was unfortunately lost. The determination of the tungsten resulted as follows: 0.4351 gram of material gave 0.1222 gram of tungsten or 28.08 per cent.

A third preparation was made. On subjecting 0.1775 gram of it to analysis these results were obtained:

0.0496 gram tungsten or 27.94 per cent.
0.1266 gram bromine or 71.32 per cent.

Tabulating the series, we have:

	Found.			Mean	Required for hexabromide.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Tungsten	27.43	28.08	27.94	27.81	27.72
Bromine	73.53	71.32	....	72.33	72.28

These figures give evidence that the body analyzed is tungsten hexabromide.

In analyzing the third portion of the blue-black needles the bromine was determined by placing the material in a small Erlenmeyer bulb, covering it with nitric acid and then distilling. The liberated bromine was passed into a silver nitrate solution.

The tungsten hexabromide prepared by us consists, as already observed, of blue-black needles. Moderately elevated temperatures decompose the compound. It gives off fumes when brought in contact with the air. Water decomposes it with the formation of a royal-blue colored oxide. Ammonia water dissolves it, the solution remaining colorless. A vapor density determination resulted negatively, as decomposition was apparent early in the experiment.

NOTES ON THE FERROCYANIDES OF ZINC AND MANGANESE.

BY EDMUND H. MILLER.

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THE composition of the ferrocyanides of zinc and manganese, formed when salts of these metals are precipitated by potassium ferrocyanide, is given by Prescott and Johnson[1] as $Zn_2Fe(CN)_6$ and $Mn_2Fe(CN)_6$, while the books on volumetric analysis, such as Sutton's and Beringer's, ignore the composition of this precipitate.

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[1] Qualitative Analysis, pages 67 and 57.