[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Tungsten Fluorides and Related Compounds[1a]

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The only well-established compounds of tungsten and fluorine thus far reported appear to be the hexafluoride and the oxytetrafluoride, prepared by Ruff and his co-workers.[1] In addition, Marignac[2] and Li[3] have indicated the existence of certain complex fluorides containing tungsten, represented by such formulas as $3NH_4F \cdot WO_3$ and $KF \cdot WO_2F_2 \cdot H_2O$, but these substances have received no detailed study. With the aim of establishing the existence of other fluorides or oxyfluorides of tungsten, the present investigation was undertaken, and as a result the tetrafluoride, WF_4, and the monoxydifluoride, WOF_2, have been prepared and analyzed, and the existence of a series of complex fluotungstic acids, represented by the formula $aWO_2 \cdot bWO_3 \cdot cHF$, has been indicated.

Tungsten Tetrafluoride.—Although the reaction represented by the equation $MO_2 + 4HF \rightarrow MF_4 + 2H_2O$ is of a type which has proved successful in the preparation of various metal fluorides, when applied to the preparation of tungsten tetrafluoride, the desired result was not obtained, but instead, as described below, the remarkably inert monoxydifluoride, WOF_2, was obtained as well as a series of blue, lustrous solids which are believed to be complex fluotungstic acids of somewhat variable composition.

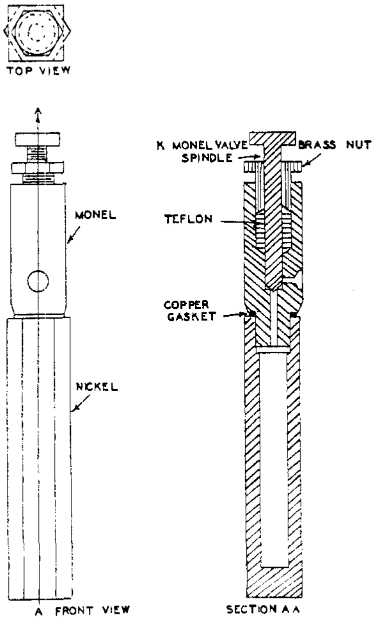

Fig. 1.—Nickel bomb.

The tetrafluoride was obtained, however, by reduction of the hexafluoride with benzene in a nickel bomb (see Fig. 1) at 110°, over a period of three to nine days. The process consisted of filling the clean, dry bomb (capacity 6 cc.) half full of dry benzene, closing the bomb and attaching to a vacuum manifold, and, after chilling to −78°, evacuating. From 1 to 1.5 g. of hexafluoride, prepared by the reaction of tungsten with fluorine and purified by distillation, was then distilled into the bomb, which was later removed from the manifold and heated in an oven at 110°. After the heating period the bomb was cooled to room temperature, the excess tungsten hexafluoride allowed to escape in a hood and the benzene pumped off with a Hyvac pump. The bomb was opened in a manipulation box containing a dry atmosphere and the product was transferred to a glass weighing bottle. The yield of tetrafluoride was approximately 20%. *Anal.* Calcd.: W, 70.76; F, 29.24. Found: W, 70.05, 69.95, 69.70; F, 29.80, 29.93, 29.24.

The compound WF_4 is a reddish-brown solid, somewhat hygroscopic; it is hydrolyzed by hot alkali solutions, precipitating brown, hydrous tungsten dioxide. Oxidizing agents in the presence of acid convert the tetrafluoride to tungsten trioxide. When heated ***in vacuo*** the compound appears to decompose, rather than melt, at temperatures approaching 800°.

Tungsten Oxyfluorides.—In the study of the reaction of tungsten dioxide with anhydrous hydrofluoric acid from 300–800°, the dioxide (prepared from Coleman and Bell C. P. tungstic acid by reduction with hydrogen at 850°) was heated in a nickel boat in a Monel reaction tube placed in an electric furnace (see Fig. 2). A trap at the outlet of the reactor was provided to collect the volatile products (Fig. 3). When the reaction was run at 500–650° for two to three hours, a gray powder was formed invariably on the surface of the tungsten dioxide. This intermediate product was separated in a "dry box" from the dioxide and analyzed: Calcd.: W, 77.30; F, 15.97. Found: W, 77.40, 77.38, 77.33, 77.67; F, 15.67, 16.00. This compound is remarkable both because of its chemical inertness and its physical resemblance to graphite or molybdenite when compacted in a mortar. It resists boiling solutions of dilute or concentrated alkali, or of concentrated sulfuric acid, hydrochloric acid, nitric acid or aqua regia. Preparation for analysis was accomplished by use of a Parr peroxide bomb, using benzoic acid as the fuel. Ignition at 700° in platinum converted the substance to tungsten trioxide. The indications are that this compound constitutes an intermediate product between the dioxide and the tetrafluoride, resulting from the reaction $WO_2 + 2HF \rightarrow WOF_2 + H_2O$.

The volatile products from the continued action of anhydrous hydrofluoric acid upon tungsten dioxide were collected, together with much unchanged hydrofluoric acid, in a nickel trap connected to the exit of the reactor. When the excess hydrofluoric acid was pumped off with a Hyvac pump, blue, lustrous solids remained, analysis of six samples of which gave: W, 73.9 ± 1.2; F, 5.66 ± 0.3. Two other samples obtained from the reaction of tungsten trioxide with anhydrous hydrogen fluoride gave similar results for tungsten: W, 73.87, 73.38; while a third, bright blue sample, prepared below 300°, gave: W, 76.6; F, 7.49. Furthermore, two samples resulting from the reaction of the trioxide with 48% aqueous hydrofluoric acid solution were found to contain W, 75.52 ± 0.01. The bright blue sample corresponds reasonably well to the requirements of the empirical formula $W_2O_5 \cdot 2HF$ (Calcd.: W, 75.40; F, 7.79), wherein tetravalent and

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[1a] This paper was presented at the meeting of the American Chemical Society, held in Chicago, April 19 to 23, 1948.

[1] Ruff, Eisner and Heller, *Z. anorg. u. allgem. Chem.*, **52**, 256 (1907); Ruff and Ascher, *ibid.*, **196**, 413 (1931).

[2] Marignac, *Ann. chim. et phys.*, [3] **69**, 63 (1863).

[3] Li and Wong, "Tungsten," Reinhold Publ. Corp., New York, N. Y., (1947) pp. 273.

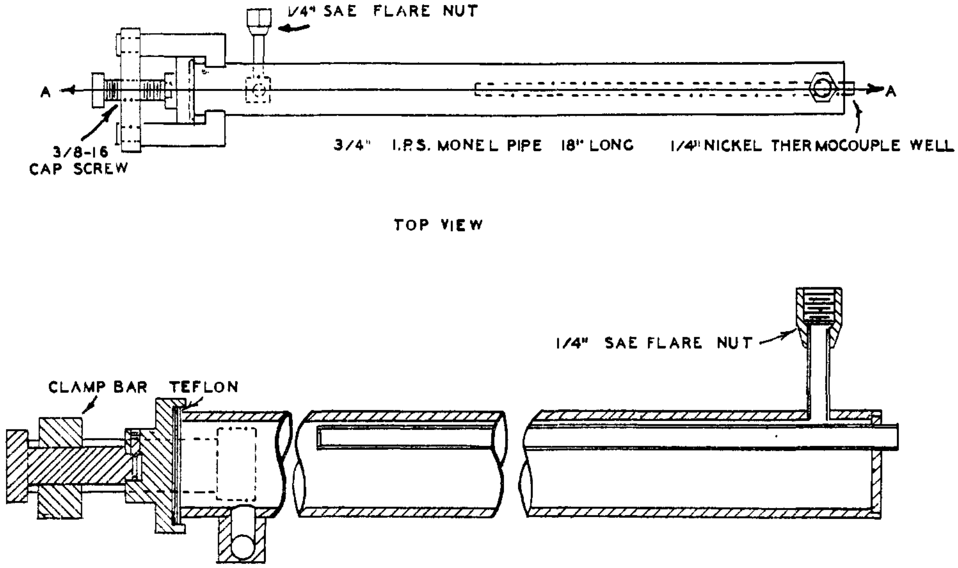


Fig. 2.

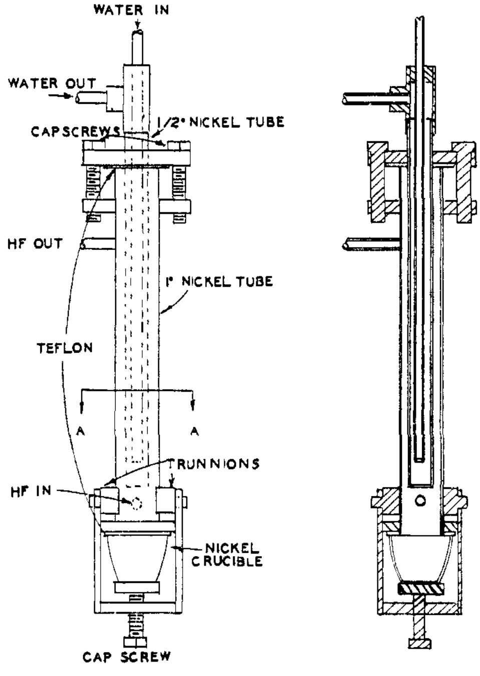
hexavalent tungsten are present. The analyses of the other samples are not greatly discordant with the requirements of the formula $W_2O_5 \cdot HF \cdot H_2O$ (Calcd.: W, 75.51; F, 3.91); from which results it may reasonably be concluded that these preparations represent mixtures of members of a series of complex acids, more or less hydrated, of tetravalent and hexavalent tungsten, represented by a general formula, $aWO_2 \cdot bWO_3 \cdot cHF$.

It is interesting to note that the X-ray diffraction patterns of these substances were found to be characteristic of the cubic perovskite structure, resembling in this respect some of the tungsten bronzes. The unit cell edges measured 3.77 Å. for the $W_2O_5 \cdot HF \cdot H_2O$ preparation, 3.84 Å. for the $W_2O_5 \cdot 2HF$ compound. These substances form ink-like blue solutions in water and are soluble in alkali, but insoluble in acid solutions. Acid solutions of oxidizing agents convert them into $WO_3 \cdot H_2O$. They ignite in air at 700° to tungsten trioxide. Glass containers are etched when these substances are stored therein, showing that a certain partial pressure of hydrogen fluoride is established by the compounds.

Summary

Although attempts to prepare tungsten tetrafluoride by the reaction of the dioxide with anhydrous hydrofluoric acid at 300–800° gave unsatisfactory results, the reaction at 500° yielded an intermediate product, WOF_2, a gray solid which compacted to shiny, black flakes resembling graphite when rubbed in a mortar. The compound is chemically inert, resisting boiling alkali or concentrated acids, even aqua regia. Ignition at 700° in platinum forms the trioxide.

Volatile by-products of this reaction were collected and yielded lustrous blue solids, analysis of which gave results indicating that they are mixtures of members of a series of fluotungstic acids, more or less hydrated, containing tetravalent and hexavalent tungsten, represented empirically by the expression $aWO_2 \cdot bWO_3 \cdot cHF$. X-Ray diffraction patterns of these solids revealed the cubic perovskite structure.



Front view Section AA

Fig. 3.

Tungsten tetrafluoride, WF_4, was prepared by reduction of the hexafluoride with benzene in a nickel bomb at 110° over a period of three to nine days. It is a reddish-brown solid, somewhat hygroscopic, hydrolyzed by hot alkali to form hydrous tungsten dioxide, and oxidized in the presence of acid to tungsten trioxide.

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