Zirconium was determined by precipitation with mandelic acid after slow solution in sulfuric acid.[7]

Anal. Calcd. for ZrF_4: Zr, 54.6. Found: Zr, 53.7, 54.4, 55.0.

Vanadium was determined by precipitation with cupferron.[8]

Fluoride was determined by thorium nitrate titration after separation by distillation.[9] The original sample was fused with sodium hydroxide, treated with water, filtered, and the filtrate distilled.

Anal. Calcd. for VOF_3: V, 41.1; F, 46.0. Found: V, 42.2, 41.1, 40.7; F, 45.0.

---

(7) C. A. Kumins, *Anal. Chem.*, **19**, 376 (1947).

(8) G. E. F. Lundell, J. I. Hoffman and H. A. Bright, "Chemical Analysis of Iron and Steel," John Wiley and Sons, Inc., New York, N. Y., 1931, p. 78.

(9) W. R. Huckabay, E. T. Welch and A. V. Metler, *Anal. Chem.* **19**, 154 (1947).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NEW HAMPSHIRE
DURHAM, NEW HAMPSHIRE

The Reaction of Fluorine with Copper and Some of its Compounds. Some Properties of Copper(II) Fluoride[1]

BY H. M. HAENDLER, L. H. TOWLE, E. F. BENNETT AND W. L. PATTERSON, JR.

RECEIVED NOVEMBER 10, 1953

The action of fluorine on copper and several of its compounds is summarized in Table I. Copper(II) fluoride was formed in all cases.

TABLE I

FLUORINATION SUMMARY

Substance	Temp., °C.	Maximum conversion, %	Remarks
Cu	500	53	*a*
Cu_2O	150–325	. . .	*b*
	325–500	. . .	*c*
CuO	300–500	65	
$CuBr_2$	25–450	98	*d*
CuCl	100–550	~100	*e*
$CuCl_2$	200–550	~100	*f*
Cu_2S	25–550	5–100	*g*
CuS	25–550	~100	
$CuSO_4$	150–550	~100	*h*

[a] Resistant fluoride coating at lower temperatures, fusion and volatilization at higher. [b] X-Ray patterns showed Cu_2O, CuO and CuF_2 in mixture; see Fig. 1. [c] CuO in mixture began to react at about 300°. [d] Three refluorinations reduced bromide content to $< 0.15\%$. [e] Chloride present at 325°, absent at 550° after refluorination. [f] 94% conversion at 325°, chloride absent at 550° after refluorination. [g] 84% conversion at room temperature with undiluted fluorine; diluted fluorine gave 5, 20 and 63%, with X-ray patterns showing only Cu_2S and CuF_2. Refluorination at 550° gave sulfide-free product. [h] 4% conversion at 150°, 20% at 250°, 74% at 325°; sulfate-free after refluorination at 550°.

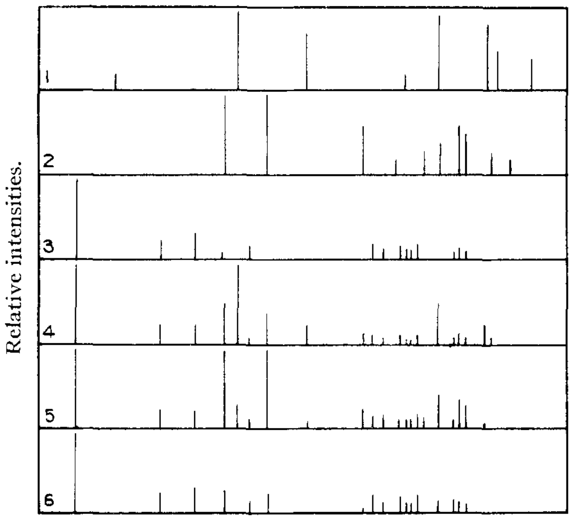

Fig. 1.—X-Ray pattern comparison for Cu_2O fluorination: 1, Cu_2O; 2, CuO; 3, CuF_2; 4, $Cu_2O + F_2$ at 200°; 5, $Cu_2O + F_2$ at 250°; 6, $Cu_2O + F_2$ at 325°.

The Density of Copper(II) Fluoride.—The density of copper(II) fluoride has been reported[2] as 4.23 g./cc., under somewhat ambiguous circumstances. The density of copper(II) fluoride, determined pycnometrically in benzene, was 4.85 ± 0.05 g./cc.

The Melting Point and Thermal Behavior of Copper(II) Fluoride.—The melting point of copper(II) fluoride has been reported[3] as 950 ± 5°, in an atmosphere of hydrogen fluoride. In a nitrogen or helium atmosphere the fluoride melted at 785 ± 10°. Considerable volatilization occurred below the melting point, and it was possible to vaporize samples completely at 850° in several hours. Powder patterns of various melts prepared by rapid heating in helium to 900–1000° showed only copper(II) fluoride lines. It was not possible to locate any lines due to metallic copper, although the position of these lines is not too favorable for distinction from the fluorides. This is in contrast to the reported formation of copper(I) fluoride[3] and subsequent disproportionation to copper and copper(II) fluoride.

The reactivity of the molten fluoride makes satisfactory study difficult, but an attempt was made to follow thermal changes by means of differential thermal analysis.[4] Runs with calcium fluoride and quartz powder as the supporting medium showed an endothermic peak at 770°, an exothermic peak at 780°, and a gradual, but very marked, endothermic change to 870–900°. This pattern suggests the possibility that copper(II) fluoride melts at 770°, decomposes at 780°, and that its decomposition product melts near 900°. At higher temperatures only calcium fluoride remained in the cell.

It was found that copper(II) fluoride reacted readily with nickel in helium at 900–950°. X-Ray powder patterns of the product showed only lines of copper and nickel(II) fluoride, in approximately equivalent amounts.

The Powder Pattern of Copper(II) Fluoride.—The crystal structure of copper(II) fluoride has been reported as the cubic fluorite type by Ebert and Woitinek,[2] although von Wartenberg[3] believed it to be of lower symmetry. X-Ray powder patterns have been made of the product of each reaction discussed above, and they are identical, re-

---

(1) Research supported by the Research Corporation and the Atomic Energy Commission.

(2) F. Ebert and H. Woitinek, *Z. anorg. Chem.*, **210**, 269 (1933).

(3) H. von Wartenberg, *ibid.*, **241**, 381 (1939).

(4) We are indebted to Danford G. Kelley, Geology Department, Massachusetts Institute of Technology, for these thermal analyses.

gardless of the method of preparation. The pattern is not that of a cubic substance.

Ebert and Woitinek prepared their material by treating massive copper with a mixture of chlorine and fluorine at 350°, assuming the layer adjacent to the copper to be copper(I) fluoride. No other experimental details or analyses of the preparations are given.

The copper(I) fluoride is given as having the zincblende structure, $F\bar{4}3m$, T_d^2, with $a_0 = 4.26$ Å.; the copper(II) fluoride, Fm3m, O_h^5, $a_0 = 5.41$ Å. The interplanar spacings for each of these structures have been calculated from these data and are shown in Table II. For comparison, the larger interplanar spacings found for copper(II) fluoride in this research are given, as are the values for copper(I) oxide and copper(I) chloride. The reported structure for copper(I) fluoride was apparently based on measurements of a red copper(I) oxide layer formed on the massive copper, possibly by contaminated gas or by air exposure on cooling. The structure of copper(II) fluoride was apparently based on measurements made with a white copper(I) chloride deposit.

TABLE II

INTERPLANAR SPACING COMPARISON

CuF_2 (this research), *d*, Å.	Relative intensity I/I_0	CuF_2 (Ebert and Woitinek) *d*, Å.	$CuCl$[5] *d*, Å.	CuF (Ebert and Woitinek) *d*, Å.	Cu_2O[5] *d*, Å.
3.22	100	3.12	3.12	2.46	2.45
2.82	25	2.70	2.70	2.13	2.12
2.66	35	1.91	1.91	1.51	1.51
2.53	8	1.63	1.63	1.28	1.28
2.39	15	1.56	..	1.22	1.23
2.28	8	1.35	1.35	1.06	1.07
2.21	8	1.24	1.24	0.98	0.98
2.04	3	1.21	..	.95	.95
1.82	18	1.10	1.10	.86	.87
1.77	15	1.04	1.04	.82	.82
1.69	18				
1.66	15				
1.64	13				
1.61	20				
1.51	3				
1.44	13				
1.42	8				
1.38	10				
1.32	8				

It has been possible to pick out of the solidified copper(II) fluoride melt small crystalline fragments of clear, colorless fluoride. Weissenberg photographs of these crystals have been taken and show the copper(II) fluoride to be monoclinic.

Experimental

The fluorination apparatus and techniques were the same as those used previously.[6] The copper metal used was heated at about 350° in hydrogen for two hours prior to fluorination. Stock C.P. copper oxides and bromide were used. Copper(I) chloride was freshly prepared by reduction of copper(II) chloride.[7] Anhydrous copper(II) chloride was prepared by dehydration of the dihydrate in the reactor furnace at 300° in nitrogen. Copper(I) sulfide was prepared by reduction of copper(II) sulfide with arsenic(III) oxide,[8] the treatment being repeated. Two forms of the sulfide have been reported, the formula often approaching Cu_9S_5.[9] Analysis showed a high sulfur content so the material was heated in nitrogen at 550°. The product gave a powder pattern similar to that for α-Cu_2S, the high chalcocite form of Buerger and Buerger.

Anal. Calcd. for Cu_2S: Cu, 79.85. Found: Cu, 80.11.

The copper(II) sulfide was prepared by precipitation with hydrogen sulfide from an acidified copper(II) sulfate solution.[8] The precipitated sulfide was extracted with carbon disulfide to remove free sulfur and stored under nitrogen.

Anal. Calcd. for CuS: Cu, 66.46. Found: Cu, 65.74, 65.78, 65.70.

C.P. anhydrous copper(II) sulfate was heated in the reactor furnace in nitrogen at 250° immediately prior to fluorination.

Copper was determined as anthranilate, after digestion with nitric or sulfuric acid, on samples from sulfide and sulfate fluorinations. All transfers involving fluoride were made in a dry-box; the anhydrous fluoride is extremely hygroscopic.

Anal. Calcd. for CuF_2: Cu, 62.58. Found: (Cu_2S + F_2)Cu, 63.08, 63.03. Found: ($CuSO_4$ + F_2)Cu, 62.91, 63.08, 62.91.

The melting point was determined by the technique used for cadmium and zinc fluorides, using, however, a horizontal 28 mm. diameter combustion tube wound with 22-gage nichrome wire. The samples were placed in a platinum boat and the calibrated chromel–alumel thermocouple placed directly above the sample. Nitrogen was purified by pyrogallol, dried with anhydrone and passed over copper turnings at 350°. Helium was used after traces of oxide were found in the fused samples.

The thermal analysis apparatus used was that described by Whitehead and Breger.[10]

Samples for powder photographs were sealed in Pyrex capillaries or coated on Pyrex fibers, followed by dipping in Formvar solution for protection against moisture. Copper radiation was used with a nickel filter.

---

(5) X-Ray Diffraction Data Cards, American Society for Testing Materials, Philadelphia, Pennsylvania.

(6) H. M. Haendler, W. L. Patterson, Jr., and W. J. Bernard, THIS JOURNAL, **74**, 3167 (1952).

(7) W. C. Fernelius, Ed., "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 1.

(8) L. Vanino, "Handbuch der Präparativen Chemie," Vol. I, Enke Verlag, Stuttgart, 1925, p. 512.

(9) M. J. Buerger and N. W. Buerger, *Am. Mineral.* **29**, 55 (1944).

(10) W. L. Whitehead and I. A. Breger, *Science*, **111**, 279 (1950).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NEW HAMPSHIRE
DURHAM, NEW HAMPSHIRE

The Reaction of Fluorine with Tin, its Oxides and Sulfides[1]

BY H. M. HAENDLER, S. F. BARTRAM, W. J. BERNARD AND D. KIPPAX

RECEIVED NOVEMBER 10, 1953

A study has been made of the action of fluorine on tin, tin(II) oxide, tin(IV) oxide, tin(II) sulfide and tin(IV) sulfide similar to that reported with zinc and nickel.[2]

Mossy tin reacts completely with fluorine above 190°, forming the tetrafluoride. There is no visible reaction of fluorine with tin(II) oxide at 150°. Reaction occurs at 200°, with two distinct layers of product being formed over the black oxide substrate. The top layer is tin(IV) fluoride, the lower is tin(IV) oxide, as shown by X-ray powder pat-

---

(1) Research supported by the Research Corporation and the Atomic Energy Commission.

(2) H. M. Haendler, W. L. Patterson, Jr., and W. J. Bernard, THIS JOURNAL, **74**, 3167 (1952).