The Reaction of Fluorine with Zinc, Nickel and Some of their Binary Compounds. Some Properties of Zinc and Nickel Fluorides[1a,1b]

BY HELMUT M. HAENDLER, WILLIAM L. PATTERSON, JR., AND WALTER J. BERNARD

The reaction of fluorine with zinc, zinc oxide, zinc bromide, zinc sulfide, nickel, nickel(II) oxide, nickel(III) oxide and nickel sulfide has been investigated. Zinc fluoride and nickel(II) fluoride are the only non-volatile products observed. The crystal structures of the two fluorides have been checked and more precise lattice constants determined. Both are tetragonal; for zinc fluoride $a_0 = 4.7021 \pm 0.0003$ Å., $c_0 = 3.1328 \pm 0.0005$ Å.; for nickel fluoride $a_0 = 4.6505 \pm 0.0003$ Å., $c_0 = 3.0837 \pm 0.0005$ Å. The densities have been redetermined: for zinc fluoride $d = 5.00 \pm 0.05$ g./cc.; for nickel fluoride $d = 4.72 \pm 0.05$ g./cc. The melting point of zinc fluoride is $875 \pm 3°$.

A recent paper[2] has reported on the action of fluorine on cadmium and some of its compounds and on the properties of cadmium fluoride. Similar studies have been made of the action of fluorine on zinc and nickel and some of their compounds and of several properties of zinc and nickel fluorides. The thermodynamics of these reactions are interesting and have been discussed by Kellogg.[3]

The Reaction of Fluorine with Zinc and Some of its Compounds.—Fluorine reacts readily with zinc dust at 250°, forming zinc fluoride, but the reaction does not proceed to completion. A protective layer of fluoride on the metal surface prevents further attack. The maximum conversion obtained was about 50%.

Zinc oxide and fluorine combine to form zinc fluoride only, as shown by X-ray diffraction. The conversion, determined by weight gain, did not exceed 75% for a single fluorination at temperatures up to 550°. Three fluorinations at 550° increased the conversion to 93%.

Repeated fluorination of zinc bromide at 500° produced fluoride containing less than 0.1% of bromide. The product was ground between each fluorination.

As was the case with cadmium sulfide, zinc sulfide and fluorine react vigorously, even at room temperature. Refluorination at 500°, after grinding, produced a fluoride which gave no test for sulfide.

X-Ray powder patterns showed zinc fluoride as the only non-volatile product and all patterns were identical.

The Reaction of Fluorine with Nickel and Some of its Compounds.—Finely divided nickel was fluorinated for purposes of comparison. It was only partially reacted at 400°. It was possible to approach complete conversion by three fluorinations at 550°, the sample being ground between runs.

Nickel(II) oxide does not react appreciably with fluorine at 300°, but the reaction is almost complete (97%) at 325°. It is complete at 375°. The final product was checked by analysis and X-ray powder patterns of the incompletely fluorinated samples showed only fluoride and unreacted oxide.

It was of interest to determine the effect of fluorine on the so-called nickel(III) oxide, Ni_2O_3, with the possibility of forming a higher fluoride. There is considerable uncertainty concerning the nature of the oxide. Sidgwick[4] has reviewed the subject and concludes that higher oxides exist, but not in the anhydrous state. The results of Hüttig and Peter[5] are considered most decisive and the oxide used was prepared by their method. The formula is given as $Ni_2O_3 \cdot 3.5 \ H_2O$; the powder pattern indicates a very low degree of crystallinity. Because of the instability of the oxide at higher temperatures fluorinations were run at 25, 50 and at 25°, followed by an increase to 350°. All lines observed in the X-ray patterns could be attributed to nickel(II) fluoride.

Nickel sulfide reacts violently with fluorine at room temperature. Subsequent refluorination at 350° produced pure fluoride.

The Structure and Density of Zinc Fluoride.—Zinc fluoride has the tetragonal SnO_2 structure, with reported lattice constants of $a_0 = 4.715$ Å., $c_0 = 3.13$ Å.,[6] and $a_0 = 4.72$ Å., $c_0 = 3.14$ Å.,[7] as determined from Debye–Scherrer powder patterns. The calculated density, 4.93 g./cc., compares with reported values of 4.556,[8] 4.84,[9] 4.858[10] and 4.95 g./cc.[11]

The observed powder patterns are in agreement with those for the space group D_{4h}^{14}, P4/mnm, with $u = 0.31$. Each unit cell has two Zn^{++} ions at $(0,0,0)$ and $(1/2,1/2,1/2)$, and four F^- ions, at $\pm (u,u,0)$ and $\pm (u + 1/2, 1/2 - u, 1/2)$. The calculated and observed intensities are in agreement. Several of Ferrari's assigned hkl values are in error and have been corrected.

The lattice constants were determined more accurately by measurement of nineteen lines of a back reflection photograph. The least squares calculation and weighting procedure suggested by

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Hess[12] were used, and assignments of indices to the lines were checked by the graphical method of Taylor and Floyd.[13]

The values of the unit cell parameters are a_0 = 4.7021 ± 0.0003 Å. (standard error) and c_0 = 3.1328 ± 0.0005 Å. The average deviation of the observed $\sin^2 \theta$ from that calculated was 0.00015. The parameter u was checked by comparison of the line intensities of the 202 and 311 reflections, as used for manganese fluoride.[14] The calculated ratio 202/311 is 2.7 at u = 0.30, 6.1 at u = 0.31, and 21.2 at u = 0.32. The observed intensities were in a ratio of 6–7 to 1.

The density, calculated from these unit cell dimensions, is 4.955 g./cc., in good agreement with Klemm's value[11] of 4.95 g./cc., and our value of 5.00 ± 0.05 g./cc., determined pycnometrically in benzene.

Two of the six fluoride ions which surround each zinc ion are at 2.07 Å., four are at 2.01 Å. The two closest fluorides are at a distance of 2.51 Å., as compared to the value 2.50 Å. suggested by Pauling[15] as the F–F distance in this type of structure for $c_0/a_0 \cong 0.66$.

The Structure and Density of Nickel Fluoride.— Nickel fluoride also has the tetragonal SnO_2 structure, with reported constants, a_0 = 4.710 Å., c_0 = 3.118 Å.[6] and a_0 = 4.65 Å., c_0 = 3.08 Å.,[7] leading to calculated densities of 4.64 g./cc. and 4.82 g./cc., respectively. These compare with reported densities of 4.63 g./cc.[16] and 4.60 g./cc.[10]

The space group is the same as for zinc fluoride, D_{4h}^{14}, with u = 0.31, with two Ni^{++} ions at (0,0,0) and ($^1/_2$, $^1/_2$, $^1/_2$). Calculated intensities agree with those observed.

Measurements of thirteen back reflection lines were used to calculate lattice constants, using the same methods of calculation as for zinc fluoride. The values of the unit cell parameters are a_0 = 4.6505 ± 0.0003 Å. and c_0 = 3.0837 ± 0.0003 Å. The average deviation of $\sin^2 \theta$ was 0.00011. The intensity ratio for 202/311 is 2.2 for u = 0.30, 4.9 for u = 0.31 and 17.4 for u = 0.32. The observed intensities were in the ratio 5–6 to 1.

The density, calculated from these dimensions, is 4.814 g./cc., higher than previously reported. A

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pycnometric determination, in benzene, gave 4.72 ± 0.05 g./cc.

Two fluorides have a Ni–F distance of 2.04 Å., four are at 1.99 Å., and the smallest F–F distance is 2.50 Å.

The Melting Point of Zinc Fluoride.—Data on the melting point of zinc fluoride are not in good agreement. Carnelley[17] and Gallo[18] have reported 734° while Puschin and Baskow[19] give 872°. The melting point of zinc fluoride, in a nitrogen atmosphere, was found to be 875 ± 3°.

Experimental

Fluorine Reactions.—The apparatus and technique were the same as those used in the study of cadmium fluoride.[2] Stock C.P. zinc compounds were used. The metal was treated with hydrogen for two hours at 250° without effect on the extent of conversion. Bromide was determined by precipitation as silver bromide. A check analysis for zinc was made on the zinc sulfide fluorination product by precipitation as the anthranilate,[20] after digestion with sulfuric acid.

Anal. Calcd. for ZnF_2: Zn, 63.23. Found: Zn, 63.30, 63.18, 63.24.

Nickel was prepared in finely divided form by reduction of the C.P. oxide with hydrogen[21] at 300–350°. Nickel sulfide was prepared by precipitation with hydrogen sulfide, as described by Vanino.[22] The fluoride from the oxide fluorination was analyzed for nickel by precipitation with dimethylglyoxime after digestion with sulfuric acid.

Anal. Calcd. for NiF_2: Ni, 60.70. Found: Ni, 60.45, 60.47, 61.12, 60.90.

Crystal Structure and Density.—The methods were those previously described. The back reflection photographs of zinc fluoride were taken with a sample prepared from the bromide. Density was measured with a sample prepared from the sulfide, and this sample was also used for the melting point determination. The nickel fluoride used for lattice measurements and density was prepared from the sulfide. The film was identical with that of a fluoride prepared from oxide.

Melting Point.—The apparatus constructed for cadmium fluoride was used. The chromel–alumel thermocouple was calibrated with sodium chloride, using the technique described. The melting point of sodium chloride was taken as 800.4°.[23]

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