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THE REACTION OF FLUORINE WITH CADMIUM AND SOME OF ITS BINARY COMPOUNDS. THE CRYSTAL STRUCTURE, DENSITY, AND MELTING POINT OF CADMIUM FLUORIDE

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The Reaction of Fluorine with Cadmium and Some of its Binary Compounds. The Crystal Structure, Density, and Melting Point of Cadmium Fluoride[1]

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Abstract

The reaction of fluorine with cadmium, cadmium oxide, cadmium chloride, and cadmium sulfide has been investigated. Cadmium fluoride is the only non-volatile product formed. The crystal structure of cadmium fluoride has been checked, and a more precise lattice constant determined; $a_o = 5.3880 \pm 0.0005$ Å. The reported experimental density values have been corrected; $d = 6.33 \pm 0.06$ g/cc. The melting point of cadmium fluoride is $1049 \pm 2^{\circ}$C.

Much of the available information on the reaction of fluorine with simple inorganic substances is in the form of generalizations. Fluorine is known to react with metals, oxides, sulfides, and other halides. In many instances, however, the conditions for reaction, the possible formation of intermediate compounds, and the characterization of the products need study.

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Two recent papers[2,3] have reported on the reaction of fluorine

(2) E. E. Aynsley, R. D. Peacock, and P. L. Robinson, J. Chem. Soc., 1622 (1950)

(3) M. Griffel and J. W. Stout, This Journal, 72, 4351 (1950)

with oxides of manganese and rhenium and on a redetermination of several properties of manganous fluoride. The present paper is the first of a series of similar studies on other inorganic fluorides.

The Reaction of Fluorine with Cadmium and Some of its Compounds. - Fluorine reacts readily with granular cadmium at 250°C., forming cadmium fluoride. It was not possible, however, to convert the metal completely to fluoride. The coating of the metal surface with fluoride prevents action. At higher temperatures the large heat of reaction, about -160 k_{cal} at 227°C.[4], and the low melting

(4) L. L. Quill, "Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics", McGraw Hill, New York, 1950

point, 320°C., combine to melt and volatilize the metal. The maximum conversion obtained was about 75%.

The action of fluorine on cadmium oxide produces only cadmium fluoride, as shown by x-ray powder patterns. The conversion, as determined by weight gain, was 24% at 325°C., 26% at 400°C., 32% at 440°C., 43% at 500°C., and 54% at 570°C. Failure to obtain

complete conversion is again attributed to the fluoride coating.

Anhydrous cadmium chloride and fluorine reacted to give 98% conversion to fluoride at 450°C. Two treatments, separated by grinding of the initial product, were necessary.

The action of fluorine on cadmium sulfide is rapid, forming nearly pure fluoride even at room temperature. By grinding and refluorinating at 300°C, any remaining sulfide can be converted to the fluoride. No qualitative test for sulfide was obtained and the x-ray pattern was that of cadmium fluoride alone. The ease of reaction at low temperature is in contrast to the 200-500°C. range suggested for sulfide reactions. At higher temperatures the reaction is almost explosive.

It is interesting in this connection to compare the free energy changes for the above reaction, assuming products as shown:

	ΔF_{298} (Kcal)[4]
$Cd + F_2 \rightarrow CaF_2$	-155
$CdO + F_2 \rightarrow CdF_2 + 1/2O_2$	-101
$CdCl_2 + F_2 \rightarrow CdF_2 + Cl_2$	- 72
$CdS + 4F_2 \rightarrow CdF_2 + SF_6$	-360

The Structure and Density of Cadmium Fluoride. - Cadmium fluoride has been reported[5] to have the cubic fluorite structure,

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(5) N. H. Kolderup, Bergens Museums Arbok, Naturv. Rekke. No. 2 (1924-5); Chemical Abstracts 22, 6 (1928)

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with a lattice constant of 5.40 Å. The density calculated from this

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value is in sharp disagreement with two previously reported values, 6.64 g/cc.[6] and 5.994 g/cc.[7] A complete check of crystal structure

(6) C. Poulenc, Compt. rend., 116, 583 (1893)

(7) F. W. Clarke, Chem. News, 49, 3 (1894)

and density has been made.

The observed powder pattern is in agreement with that calculated for the fluorite structure, $F43\text{-}O^3$, with four Cd^{++} ions and eight F^- ions in each unit cell. The calculated and observed intensities are listed in Table I.

Table I.

Intensity of CdF_2 Diffraction Lines

hkl	d	intensity on arbitrary scale obs.	calcd.
111	3.103	100	100
200	2.688	23	21
220	1.903	59	65
311	1.622	47	45
222	1.553	7	7
400	1.345	10	10
331	1.235	26	19
420	1.204	8	10
422	1.099	26	23
511-333	1.036	21	19
440	0.952	7	10
531	0.910	29	29
600-442	0.897	8	12
620	0.852	19	26
533	0.822	14	23
622	0.812	13	16

The lattice constant was determined more accurately by measurements of nine lines of a back reflection photograph. The values of a_o calculated for known hkl values, when plotted against

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$\cot\theta \cos^2\theta$ as suggested by Buerger[8], gave the extrapolated

(8) M. J. Buerger, "X-Ray Crystallography", Wiley, New York, 1942, p. 426

value $a_o = 5.3880 \pm 0.0005$ Å.

The density, calculated from the cell constant is 6.386 g/cc., compared to a value of 6.33 ± 0.06 g/cc., obtained by pycnometric measurement of the powder.

The Melting Point of Cadmium Fluoride. - Data on the melting point are confusing. Carnelley[9] gives a calculated value

(9) T. Carnelley, J. Chem. Soc. 33, 293 (1898)

of 520°C, while Puschin and Baskow[10] have reported 1110°C.

(10) N. Puschin and A. Baskow, Z. anorg. Chem. 81, 358 (1913)

The melting point of cadmium fluoride, in a nitrogen atmosphere, was found to be 1049 ± 2°C.

Experimental

Fluorine Reactions. - Fluorine, from a Harshaw laboratory-type cell, was passed thru a cold trap and an absorber containing sodium fluoride pellets at 100°C. to remove hydrogen fluoride. Reactions were carried out in a heavy-walled nickel cylinder, 12 in. long and 1 1/4 in. o.d., fitted with a thermocouple well and an external screw cap, lubricated with fluorocarbon oil[11].

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(11) DuPont FC-335 Fluorocarbon oil. B.P. 210-240°/10 mm.

The lubricant served admirably to prevent seizure of the cap threads. The reactor was heated by a standard combustion furnace, with automatic control to ±5°C. Samples were placed in weighed nickel boats. Gain in weight of the boat alone was negligible. Preheating and cooling were done in a nitrogen stream.

The cadmium metal and oxide were c. p. materials. The chloride was made by dehydration of the hydrate by fusion in platinum. The sulfide was prepared by the method given by Vanino[12], using one-tenth the suggested amount of sulfuric acid.

(12) L. Vanino, "Handbuch der Präparativen Chemie", Enke Verlag, Stuttgart, 1925, vol. I, p. 565

Crystal Structure and Density. - Powder photographs were made with precipitated material which passed 200-mesh bolting cloth. A Philips 114.59 mm. camera was used, with the rotated sample mounted on a fine Pyrex fiber. Copper radiation was used with a nickel filter. The observed intensities were compared with a standard set of films prepared by the "sandwich" technique of Robertson[13], assuming 75% absorption by each layer, as reported

(13) J. M. Robertson, J. Sci. Instruments, 20, 175 (1943)

for Eastman No-Screen film by Kaufman and Fankuchen[14].

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(14) H. S. Kaufman and I. Fankuchen, Anal. Chem., 21, 24 (1949)

The calculated intensities were obtained from standard atomic scattering factors[15], corrected for angle factor and

(15) "Int. Tabellen Bestimmung Kristallstrukturen", Borntraeger-Edwards, 1944, p. 571

multiplicity[16] and for absorption using the Claassen method[17].

(16) C. W. Bunn, "Chemical Crystallography", Oxford University Press, London, 1945, p. 207

(17) Reference (15), p. 583

The back reflection photographs were also taken with filtered copper radiation, using a Philips 12 cm. diameter precision focussing camera. The film was corrected for shrinkage using the fiduciary marks of the camera. Identical results were obtained with two samples, one from the cadmium sulfide reaction, and one from a precipitated cadmium fluoride.

The precipitated cadmium fluoride which was also used for density and melting point measurements, was prepared by a modification of the method of Nuka[18], in which a nearly boiling solution of 100 g.

(18) P. Nuka, Z. anorg. Chem., 180, 235 (1929)

of cadmium nitrate tetrahydrate and 2 drops of 6 M nitric acid in a total volume of 125 ml. was treated with a filtered solution of

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30 g. of ammonium fluoride in 75 ml. of water to which had been added enough hydrofluoric acid to make the resultant solution slightly acid. The precipitate was digested near boiling for about 15 min., before filtering and washing with warm water and ethanol. The material is microcrystalline and filters readily.

The density was determined at 25°C., using the pycnometric method given by Bauer[19]. Benzene and benzene containing Aerosol

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(19) N. Bauer in A. Weissberger, "Physical Methods of Organic Chemistry", Interscience Publishers, New York 1945, p. 99

OT[20] were used as immersion liquids. Their densities were

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(20) American Cyanamide Company

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determined by comparison with gas-free distilled water. Complete removal of air from the fine solid was extremely difficult.

Melting Point. - The melting point was determined in a graphite crucible, about 40 mm. long and 20 mm. in diameter. The crucible was supported by perforated nickel tubing inserted into a hole in the bottom. The tube and crucible were mounted in a vertical 25 mm. diameter nickel tube wound with 22-gauge nichrome wire over a 150 mm. section and well lagged with asbestos. The chromel-alumel thermocouple was introduced from the top of the furnace, and nitrogen passed in through the perforated crucible support tube during the run.

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Attempts to obtain satisfactory cooling curves were not successful because of the large volume decrease on fusion. As a result the melting point was determined by raising the furnace temperature to successive levels and ultimately determining the temperature at which the sample melted. The thermocouple was calibrated with silver by the same method in the same apparatus, taking the melting point of silver as 960.8°C.[21]

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(21) Chem. Eng. News, 27, 702 (1949)

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