[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

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

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The reaction of fluorine with cadmium, cadmium chloride, cadmium oxide 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; $a_0 = 5.3880 \pm 0.0005$ 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 ± 2°.

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.

Two recent papers[2,3] have reported on the reaction of fluorine 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°, 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 kcal. at 227°,[4] and the low melting point, 320°, 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°, 26% at 400°, 32% at 440°, 43% at 500° and 54% at 570°. 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°. 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°, 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° 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 reactions, assuming products as shown

	ΔF_{298}, kcal.[4]
$Cd + F_2 \rightarrow CdF_2$	−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, with a lattice constant of 5.40 Å. The density calculated from this 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 and density has been made.

The observed powder pattern is in agreement with that calculated for the fluorite structure, space group F43-0^3, with four Cd^{++} ions and eight F^- ions in each unit cell. The calculated and observed intensities are in close agreement.

The lattice constant was determined more accurately by measurements of nine lines of a back reflection photograph. The values of a_0 calculated for known *hkl* values, when plotted against $\cot\theta\cos^2\theta$ as suggested by Buerger,[8] gave the extrapolated value $a_0 = 5.3880 \pm 0.0005$ 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 of 520°, while Puschin and Baskow[10] have reported 1110°. The melting point of cadmium fluoride, in a nitrogen atmosphere, was found to be 1049 ± 2°.

Experimental

Fluorine Reactions.—Fluorine, from a Harshaw laboratory-type cell, was passed through a cold trap and an absorber containing sodium fluoride pellets at 100° 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, lubri-

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(1) (a) This work is part of a program of research in inorganic fluorides supported by the Research Corporation and the Atomic Energy Commission and is taken in part from the B.S. and M.S. theses of W. J. Bernard. (b) For a table summarizing the X-ray data order Document 3306 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

(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).

(4) L. L. Quill, "Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950.

(5) N. H. Kolderup, *Bergens Museums Aarbok, Naturvidensk. raek*, No. **2** (1924–1925); *C. A.*, **22**, 6 (1928).

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

(7) F. W. Clarke, *Chem. News*, **49**, 3 (1884).

(8) M. J. Buerger, "X-Ray Crystallography," John Wiley and Sons, Inc., New York, N. Y., 1942, p. 426.

(9) T. Carnelley, *J. Chem. Soc.*, **33**, 273 (1898).

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

cated with fluorocarbon oil.[11] 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°. 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.

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

The calculated intensities were obtained from standard atomic scattering factors,[15] corrected for angle factor and multiplicity[16] and for absorption using the Claassen method.[17]

The back reflection photographs were also taken with filtered copper radiation, using a Philips 12-cm.-diameter precision focusing 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. 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 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°, using the pycnometric method given by Bauer.[19] Benzene and benzene containing Aerosol OT[20] were used as immersion liquids. Their densities were 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-gage 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.

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°.[21]

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[11] du Pont FC-335, fluorocarbon oil, b.p. 210–240° (10 mm.).

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

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

[15] "Int. Tabellen Bestimmung Kristallstrukturen," Borntraeger-Edwards, 1944, p. 571.

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

[17] Reference (15), p. 583.

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

[20] American Cyanamid Company.

[21] *Chem. Eng. News*, **27**, 702 (1949).

[Contribution from the Coates Chemical Laboratory, Louisiana State University]

A Theory of Irreversible Polarographic Waves[1,2]

By Paul Delahay and Jacob E. Strassner

An equation for irreversible polarographic waves is derived by assuming that the current at any point of the wave is controlled by the rate of the electrode process and by the rate of diffusion of the substance reacting at the electrode. The dependence of the rate constant for the electrode process on the potential of the dropping mercury electrode is interpreted on the basis of the theory of absolute rates. The free energy of activation and the transfer coefficient for a given electrode reaction are computed from the corresponding current-voltage curve. The theory is applied to the reduction of iodate ion, and some experimental factors that might possibly affect the rate of electrode processes are examined. Relatively large variations of the rate of the electrode process are caused by the addition of gelatin. The number of electrons involved in the rate determining step of the reduction of iodate ion is calculated for solutions of various pH.

Although several treatments of irreversible waves have been reported[3-6] in the recent years, there is still a need for a satisfactory theory of these waves, as pointed out by Laitinen.[7] In the present paper, we report a new theory of irreversible waves which was developed by assuming that the current at any point of an irreversible wave is controlled by the rate of the electrode process and by the rate of diffusion of the substance reacting at the electrode.

General Equation for Irreversible Waves

We consider the case of an irreversible cathodic wave corresponding to an electrode process of the first order. Moreover, we assume that the influence of the reverse anodic process is negligible. This assumption is valid, provided that the cathodic overvoltage is at least a few tenths of a volt. No serious limitation is introduced by this condition, since many irreversible waves actually involve overvoltages of at least half a volt. Under these

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[1] Paper presented before the Division of Physical and Inorganic Chemistry of the XIIth International Congress of Pure and Applied Chemistry held in New York in September, 1951.

[2] Abstracted from a thesis to be submitted by J. E. Strassner in partial fulfillment of the requirements for the degree of Master of Science.

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[7] H. A. Laitinen, in "Annual Review of Physical Chemistry," G. K. Rollefson, and R. E. Powell, Editors, Annual Reviews, Inc., Stanford, California, 1950, Vol. I, p. 307.