cm.$^{-1}$ (ν_3) according to the assignment of Burke, *et al.*[26]

Further evidence that these solids are ionic compounds is provided by their X-ray diffraction data. Musil, *et al.*,[12] have shown that the solids have pseudo-cubic crystal structures. Although the structures of these compounds have not been fully elucidated due to lack of single crystal X-ray data, it has been clearly demonstrated that the gross geometrical arrangement involves an NO^+ ion in the center of a cube with MF_6^- ions at the corners.

The failure of nitric oxide to react with tungsten hexafluoride to form $NOWF_6$ was unexpected, especially since the pentavalent complex fluorotungstates of sodium and potassium already have been prepared.[27] The potassium salt (KWF_6) has an infrared absorption band at 594 cm.$^{-1}$ attributed to ν_3 vibration of the WF_6^- ion.[25] Also, nitrosyl pentavalent complex fluorides of all of the group V-B elements have been prepared.[5] We have no explanation for the lack of reactivity of tungsten hexafluoride with nitric oxide.

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[26] T. G. Burke, D. F. Smith, and A. H. Nielsen, *J. Chem. Phys.*, **20**, 447 (1952).

[27] G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.*, 4212 (1957).

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Phase Equilibria in the System Chromium(II) Fluoride–Chromium(III) Fluoride

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An investigation of the CrF_2–CrF_3 system established the existence of a single chromium(II,III) fluoride covering the solid solution range $CrF_{2.40}$ to $CrF_{2.45}$. There are two invariant points, the eutectic at 831 ± 5° containing 14 mole % CrF_3 and the peritectic at 997 ± 5° containing 29 mole % CrF_3. CrF_3 forms a solid solution containing 10 mole % CrF_2. Melting points of the components CrF_2 and CrF_3, both previously reported to be 1100°, were determined to be 894 ± 6° and 1404 ± 20°, respectively. Because classical procedures yielded mixed products, new methods of synthesizing CrF_2 were sought. Five new procedures are reported: (1) disproportionation of CrF_3 at 1100°, (2) pyrolysis of $(NH_4)_3CrF_6$, (3) reduction of CrF_3 with Cr^0 at 1100°, (4) reduction of $CrCl_3$ with molten SnF_2, and (5) oxidation of Cr^0 with a molten fluoride of a more noble metal, SnF_2, PbF_2, CuF_2, CdF_2, or BiF_3. $(NH_4)_3CrF_6$ for the preparation of CrF_3 and CrF_2 has been synthesized by the reaction of molten NH_4HF_2 with $CrF_3 \cdot 3H_2O$, CrO_3, or $(NH_4)_2Cr_2O_7$. The compound chromium(II,III) fluoride, previously unreported, was encountered when the disproportionation of CrF_3 was incomplete, when CrF_3 was partially reduced by hydrogen, and when CrF_2 was oxidized by HF or SnF_2. The compound forms green, translucent crystals that are biaxial (−) with refractive indices $N_\alpha = 1.518$ and $N_\gamma = 1.534$.

Introduction

Extensive studies at the Oak Ridge National Laboratory[2] of the corrosion of chromium alloy containers by molten fluorides have depended on a source of pure, anhydrous CrF_2. New methods for synthesizing CrF_2 were investigated when the necessary large quantities could not be obtained readily in sufficient purity by the usual procedures. In the course of this investigation, chromium(II,III) fluoride, a compound previously unreported, was encountered and studied. Interest in this compound stimulated a complete study of the CrF_2–CrF_3 system.

Chromium(II) fluoride is known only in the form of the anhydrous salt. It first was reported

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[1] Operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

[2] (a) Molten-Salt Reactor Program Quarterly Progress Report for Period Ending January 31, 1958, U. S. Atomic Energy Commission ORNL-2474, pp. 104–111; (b) R. B. Evans III, J. H. DeVan, and G. M. Watson, "Self-Diffusion of Chromium in Nickel-Base Alloys," U. S. Atomic Energy Commission ORNL-2982, Jan. 20, 1961.

by Poulenc,[3,4] who obtained it by passing anhydrous HF gas over red hot chromium metal or anhydrous $CrCl_2$ at the "ordinary" temperature, presumably room temperature. These hydrofluorination reactions persist as the usual prescribed procedures for preparing CrF_2.[5-8] Jack and Maitland[9] so prepared the compound from $CrCl_2$. When Muetterties and Castle[10] hydrofluorinated the metal, they obtained CrF_2 at 900°, but CrF_3 at 300°. Mourlot[11] allowed CrS to react with HF to form a solid which he assumed to be CrF_2. Jellinek and Rudat[12] prepared CrF_2 by the hydrogen reduction of CrF_3 at elevated temperatures.

Evaluation of Classical Methods of Preparing Chromium(II) Fluoride

1. Hydrogen Fluoride Reactions. Chromium Metal.—Several attempts were made to prepare CrF_2 by allowing chromium metal to react with hydrogen fluoride gas at 800° in a nickel vessel. The reaction vessel was a cylinder made by welding a 0.635-cm. plate, serving as the bottom, over one opening of a 15.2-cm. length of standard 10.2-cm. pipe. The other end had a lid provided with the gas exit line and the gas inlet tube which extended nearly to the bottom of the vessel.

None of the attempts yielded a satisfactory product. When finer than 325-mesh the chromium powder became cemented together by the treatment so as to plug the apparatus. The use of 100-mesh chromium served to avoid plugging, but the reaction was incomplete because the particles of metal became coated with a green product which inhibited further reaction. Grinding removed this layer so more chromium could be attacked, but three successive treatments left much metal still unreacted. The green product was shown by X-ray diffraction analyses to be principally chromium(II,III) fluoride but containing also some CrF_2 and CrF_3.

Chromium(II) Chloride.—Attempts were made to prepare CrF_2 from $CrCl_2$ by the procedure used by Poulenc.[3,4] Chromium(II) chloride was allowed to react with HF gas at room temperature on the assumption that this was his reported "ordinary" temperature. Under these conditions, however, HF was absorbed by the $CrCl_2$ to form a dark green solution. (Dissolved chromium chloride raised the boiling point of HF sufficiently to allow the liquid to form at room temperature.) It was necessary to heat the $CrCl_2$ during the hydrofluorination in order to obtain a solid product.

In a reaction vessel like that used for treating chromium metal, C.P. grade $CrCl_2$ obtained from Fisher Scientific Company (Cat. No. C326) was hydrofluorinated at temperatures of 300–700°. Although HF was passed through the $CrCl_2$ until no chloride could be detected with aqueous $AgNO_3$ in the spent gas, the green solid obtained as the product contained about 0.2% chloride. The X-ray diffraction patterns indicated that the product contained approximately equal amounts of CrF_2, CrF_3, and chromium(II,III) fluoride.

Effect of Hydrogen Fluoride on Chromium(II) Fluoride.—The formation of trivalent chromium during hydrofluorination of chromium metal or $CrCl_2$ apparently results from the oxidation of CrF_2 by HF. By treatment with HF at 300–350° for 2-1/3 hr., pure CrF_2, made by fusing SnF_2 with chromium metal, became contaminated with 30% CrF_3 and 20% chromium(II,III) fluoride due to the reaction

$$2CrF_2 + 2HF \longrightarrow 2CrF_3 + H_2$$

According to Glassner's[13] free energy values, this reaction, the reverse of that used by Jellinek[12] to prepare CrF_2, is favored by approximately 12 kcal. Three different phases were present because the hydrogen fluoride gas, as in the case of the treatment of chromium metal, did not penetrate the salt well enough to make the product uniform.

2. Hydrogen Reduction of Chromium(III) Fluoride.—Batches of 200 to 400 g. of CrF_2 were prepared by hydrogen reduction of CrF_3 in a nickel reaction vessel like that used above for hydrogen fluoride reactions. The hydrogen flow was regulated to maintain a flame with the gas stream leaving the reaction vessel. The reduction occurred only very slowly below 600°, but rapidly above 800° with noticeable evolution of heat. For convenience and control of the reaction a temperature of 725° was preferred.

Usually the resulting CrF_2 was seriously contaminated with chromium metal due to the reaction

$$CrF_2 + H_2 \longrightarrow Cr^0 + 2HF$$

In order to obtain a pure product the reduction must be stopped after eliminating trivalent chromium but before forming metal. No method was devised to determine when this had occurred. Non-uniformity of temperature due to external heating with an electric furnace makes the metal formation especially difficult to avoid. Both the reduction of CrF_3 to CrF_2 and the further reduction to metal, according to published free energy values,[13] are favored by a rise in temperature; therefore, more reduction takes place in the hotter portion of the material near the container wall. The CrF_2 formed in the hotter regions was contaminated with chromium metal, sometimes in sufficient concentration to be detected by X-ray diffraction.[14] (Similar contamination by metallic chromium was encountered in the preparation of $CrCl_2$ by hy-

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(3) M. C. Poulenc, *Compt. rend.*, **116**, 253 (1893).

(4) M. C. Poulenc, *Ann. Chim. Phys.*, (7) **2**, 60 (1894).

(5) J. R. Partington, "Textbook of Inorganic Chemistry," The Macmillan Co., London, 6th ed., 1958, p. 884.

(6) R. N. Haszeldine and A. G. Sharpe, "Fluorine and Its Compounds," Methuen, London, pp. 50–51.

(7) J. N. Friend, "Textbook of Inorganic Chemistry," Vol. VII, Part III, Griffin, London, 1926, p. 22.

(8) E. de Barry Barnett and C. L. Wilson, "Inorganic Chemistry," Longmans, Green and Co., London, 2nd ed., 1957, p. 190.

(9) K. H. Jack and R. Maitland, *Proc. Chem. Soc.*, 232 (1957).

(10) E. L. Muetterties and J. E. Castle, *J. Inorg. Nucl. Chem.*, **18**, 148 (1961).

(11) A. Mourlot, *Ann. Chim. Phys.*, (7) **17**, 544 (1899).

(12) K. Jellinek and A. Rudat, *Z. anorg. allgem. Chem.*, **175**, 281 (1928).

(13) A. Glassner, "The Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500°K," U. S. Atomic Energy Commission ANL-5750, 1957.

(14) American Society for Testing Materials, Chromium, X-Ray Diffraction Data Card No. 6-0694.

drogenation of $CrCl_3$.[15]) The nickel of the container did not seem to catalyze the reduction, as chromium still tended to form near the metal surfaces when the vessel was plated with chromium or lined with silver. If the reduction was inadequate to form CrF_2, chromium(II, III) fluoride was found.

Good CrF_2 sometimes was obtained by mechanically separating uncontaminated portions of a batch. Usually the material was over-reduced with the intention of leaving no trivalent chromium, and then purified by recrystallizing. This was done by fusing in a graphite crucible and selecting clear crystals.

The recrystallization removed not only the free metal but also the traces of CrN[16] introduced with CrF_3 made by decomposing $(NH_4)_3CrF_6$. Direct hydrogenation of $(NH_4)_3CrF_6$ eliminated the need to prepare CrF_3, but shifted the reaction to increase the CrN contamination of CrF_2. Being opaque, CrN interfered with optical evaluation of the product.

New Methods of Preparing Chromium(II) Fluoride

1. **Pyrolysis of AmmoniumHexafluorochromate (III).**—Heating 30 to 60 g. portions of $(NH_4)_3CrF_6$ for 5 hr. at 1100° in a graphite crucible was found to be a convenient procedure for preparing small quantities of CrF_2.

The formation of CrF_2 by the pyrolysis of $(NH_4)_3CrF_6$ is explained as follows: Decomposition of $(NH_4)_3CrF_6$ at 450° forms CrF_3, part of which is reduced to the chromous state by hydrogen, a volatile product of the decomposition. At higher temperatures the remaining CrF_3 disproportionates to form molten CrF_2 and a volatile higher chromium fluoride, a reaction which is treated next as a method of preparing CrF_2.

While a helium atmosphere sometimes was provided during the pyrolysis, it was found not to be necessary. The decomposing fluorochromate provided large volumes of gaseous hydrogen fluoride, ammonia, hydrogen, and nitrogen, which displaced the air from the container and protected the product. The crucible was provided with a cover that was loose so it could be lifted by inside pressure to permit the escape of gaseous decomposition products.

To go to completion, the reaction depends on the removal of the volatile higher fluoride of chromium. As the effectiveness of this removal is influenced by the geometry of the charge and time, the procedure was not applicable to batches larger than approximately 25 g. The reaction also depends on temperature. Attempts at making larger batches or using lower temperatures resulted in products badly contaminated with chromium(II,III) fluoride.

2. **Disproportionation of Chromium(III) Fluoride.**—Experiments on the disproportionation of CrF_2 were initiated to study the mechanism of $(NH_4)_3CrF_6$ pyrolysis. The disproportionation of CrF_3 itself served also as a new useful method of preparing CrF_2.

A graphite crucible containing 26 g. of anhydrous CrF_3 powder and a platinum crucible with 3.77 g. of the powder, both with loose fitting lids, were heated for 4 hr. at 1100°. On cooling each crucible contained a button of well crystallized CrF_2 in yields corresponding to weight losses of 49 and 45.8%, respectively. The loss of weight in the platinum crucible is in reasonable agreement with the 44.9% loss of weight required for the disproportionation reaction

$$3CrF_3 \longrightarrow 2CrF_2 + CrF_5\,(g)$$

The volatile product, CrF_5, has been described by von Wartenberg.[17]

The slightly lower yield in the graphite crucible presumably was due to some loss of CrF_2 vapors through the porous graphite. Because the yield was no higher, the reaction of graphite with CrF_3 could not be a significant factor in the formation of CrF_2.

Like the pyrolysis procedure, the disproportionation of CrF_3 was useful for preparing only small batches of CrF_2.

3. **Reaction of Chromium(III) Fluoride with Chromium Metal.**—The reaction

$$Cr^0 + 2CrF_3 \longrightarrow 3CrF_2$$

produced pure CrF_2 at 1000° when the intimately mixed reacting powders were sealed in an evacuated 2.54 cm. o.d. nickel tube. A contaminant, 0.2% nickel, found by spectroscopic analysis, presumably was due to corrosion of the container.

4. **Reduction of Chromium(III) Chloride with Tin(II) Fluoride.**—Chromium(II) fluoride formed when equal moles of anhydrous $CrCl_3$ and SnF_2 were heated slowly to 1100° in a graphite crucible. The mixture of reactants was compressed at 8000 p.s.i. to eliminate air, which otherwise would contaminate the product with oxides. Some loss of product occurred due to seepage through the crucible. The volatile products were presumed to be $SnCl_4$, boiling at 114°,[18] and $SnCl_2$, boiling at 623°.

$$2SnF_2 + 2CrCl_3 \rightarrow SnCl_4\,(g) + SnCl_2\,(g) + 2CrF_2$$

The residue of CrF_2 was contaminated with 2.5 to 7% chloride.

5. **Reaction of Chromium(II) Chloride with Tin(II) Fluoride.**—Similar to the reaction with $CrCl_3$, SnF_2 converted $CrCl_2$ into impure CrF_2.

$$CrCl_2 + SnF_2 \longrightarrow CrF_2 + SnCl_2\,(g)$$

6. **Oxidation of Chromium Metal with Fluorides of More Noble Metals.** Chromium metal was allowed to react with the molten fluorides SnF_2, BiF_3, PbF_2, CuF_2, and CdF_2, all of metals more noble than chromium, to form CrF_2 and the noble metal. These reactions and their yields of CrF_2 are

$$SnF_2\ (\text{m.p. } 213°)^{19} + Cr \longrightarrow Sn\ (\text{m.p. } 232°)^{20} + CrF_2 \qquad (95\%\ \text{yield})$$

$$2BiF_3\ (\text{m.p. } 727°)^{21} + 3Cr \longrightarrow 2Bi\ (\text{m.p. } 271.5°)^{22} + 3CrF_2 \qquad (93\%\ \text{yield})$$

$$PbF_2\ (\text{m.p. } 824°)^{21} + Cr \longrightarrow Pb\ (\text{m.p. } 327°)^{23} + CrF_2$$

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[15] A. B. Burg, "Anhydrous Chromium(II) Chloride," in "Inorganic Syntheses," Vol. III, ed. by L. F. Audrieth, McGraw-Hill, New York, N. Y., 1950, pp. 150–153.

[16] American Society for Testing Materials, Gamma Chromium Nitride, X-Ray Diffraction Data Card No. 3-1157.

[17] H. von Wartenberg, *Z. anorg. allgem. Chem.*, **247**, 135 (1941).

[18] Landolt-Börnstein, "Eigenschaften der Materie in Ihren Aggregatzuständen," Part 4, Springer, Berlin, 1961, p. 256.

$$CuF_2\ (\text{m.p. } 927°)^{21} + Cr \longrightarrow Cu\ (\text{m.p. } 1083°)^{24a} + CrF_2\quad (68\%\ \text{yield})$$

$$CdF_2\ (\text{m.p. } 1110°)^{21} + Cr \longrightarrow Cd\ (\text{b.p. } 767°)^{24b} + CrF_2\quad (93\%\ \text{yield})$$

(The melting points of the reacting fluorides are included as they represent the minimum temperatures chosen for carrying out the reactions.) Such reactions afford suitable means of preparing pure CrF_2 if it is easily separable from the resulting noble metal. In the reaction of CdF_2 with chromium metal, volatilization was so effective in removing the cadmium metal that less than 0.2% was found in the CrF_2 residue. When SnF_2 or BiF_3 reacted, the CrF_2 was effectively separated by maintaining it in the molten state (about 900°) for 2 hr. to allow the dense, immiscible liquid metal to settle. On solidifying, CrF_2 was recovered in nearly quantitative yield. Molten copper and lead did not separate as cleanly; therefore, when employing their fluorides, recovery of CrF_2 was poorer. Generally an excess of 1 or 2% chromium metal was provided to ensure the absence of chromium(II,III) fluoride in the product.

To prevent seepage of SnF_2, a high density graphite, "Graphitite,"[25] was used as the container for the reaction. The other reactions were carried out in ordinary graphite crucibles. There was some loss of molten PbF_2 through the crucible, which, with the incomplete separation of phases, resulted in a small yield of CrF_2.

One-half kg. of CrF_2 can be prepared at a time from SnF_2 and chromium in a crucible of 600 cc. capacity. Because very pure reactants are available commercially, very pure CrF_2 can be prepared by this method. Metal and Thermit SnF_2 contains less than 100 p.p.m. metallic element impurities. Electrolytic chromium powder (Belmont Smelting and Refining) contains 200 p.p.m. iron as the principal impurity. A typical batch of this CrF_2 yielded the following analysis by procedures regarded accurate within ±2%.

	Found, %	Calcd., %
Cr	56.7	57.8
F	41.2	42.2
	97.9	100.0
Ratio F/Cr	1.99	2.00

Spectroscopically, 0.1 to 0.2% Sn and 0.03% each of Fe and Ca were detected. Because of the limits of accuracy of chemical analysis, the purity was best appreciated by examination with a polarizing microscope. This showed the absence of chromium(II,III) fluoride and the presence of only insignificant amounts of opaque material.

Preparation of Chromium(III) Fluoride

Some of the CrF_3 for conversion to CrF_2 was made by decomposing $(NH_4)_3CrF_6$ at 450–550°, a modification of the procedure of Hein, Reschke, and Pintus.[26]

$$2(NH_4)_3CrF_6 \longrightarrow 2CrF_3 + 6H_2\,(g) + 3N_2\,(g) + 6HF\,(g)$$

It was necessary to flush off the volatile products with helium to prevent any reduction by the hydrogen or contamination with CrN[16] from the reaction

$$2CrF_3 + N_2 + 3H_2 \longrightarrow 2CrN + 6HF$$

Chromium(III) fluoride for the phase studies and some of that used for the preparation of CrF_2 was made by treating sublimed $CrCl_3$ with HF gas at 450–550°. Both methods were sensitive to temperature: the conversion to CrF_3 was incomplete below 450°, but contamination with chromium(II,III) fluoride occurred above 600°, apparently because of disproportionation. Most previous workers, such as von Wartenberg,[27] used higher temperatures for the conversion of $CrCl_3$ and presumably obtained contaminated products.

Chromium(III) fluoride, like CrF_2, was difficult to attack for chemical analysis; therefore, it was analyzed by the same procedures. The product used for the phase studies yielded the analysis

	Found, %	Calcd., %
Cr	47.1	47.7
F	51.6	52.3
	98.7	100.0
Ratio F/Cr	3.00	3.00

The principal impurities were 0.1% each of Fe and Cl.

Preparation of Ammonium Hexafluorochromate(III).—As the $(NH_4)_3CrF_6$ was intended for high temperature decomposition into CrF_3 or pyrolysis to form CrF_2, moisture which by hydrolysis could contaminate the products with oxide was to be avoided. The usual aqueous procedures were rejected, as $(NH_4)_3CrF_6$ readily hydrates[28] when so prepared. At 200° molten NH_4HF_2, an effective hydrofluorinating agent, served to volatilize moisture and prevent hydrolysis when employed as solvent and reactant in the reactions

$$3NH_4HF_2 + CrF_3\cdot 3H_2O \longrightarrow (NH_4)_3CrF_6 + 3H_2O\,(g) + 3HF\,(g)$$

$$8NH_4HF_2 + 2CrO_3 \longrightarrow 2(NH_4)_3CrF_6 + 4HF\,(g) + N_2\,(g) + 6H_2O\,(g)$$

$$6NH_4HF_2 + (NH_4)_2Cr_2O_7 \longrightarrow 2(NH_4)_3CrF_6 + N_2\,(g) + 7H_2O\,(g)$$

Excess NH_4HF_2 was eliminated by decompostion at 250°.

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[19] B. J. Thamer and G. E. Meadows, "The Systems UF_4–SnF_2 and PuF_3–SnF_2," U. S. Atomic Energy Comm. LA-2286 (1959); *Chem. Abstr.*, **53**, 21223c (1959).

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[22] D. R. Stuhl and G. C. Sinke, reference 20, p. 55.

[23] Reference 20, p. 117.

[24] (a) Reference 20, p. 81; (b) reference 20, p. 63.

[25] "Graphitite" is produced by Graphite Specialties Corporation, Niagara Falls, New York.

[26] F. Hein, J. Reschke, and F. Pintus, *Ber. deut. chem. Ges.*, **60B**, 679 (1927).

[27] H. von Wartenberg, *Z. anorg. allgem. Chem.*, **249**, 100 (1942).

[28] C. F. Baes, Oak Ridge National Laboratory, private communication, 1958.

Properties of Chromium(II) Fluoride

The color of CrF_2 has been reported variously as colorless,[8] white,[5] gray,[6] bluish green,[4] and green.[7] The diversity of colors probably is due to the effects of particle size and impurities. Pure CrF_2, when crystallized by fusion to form plates over 2 mm. thick, had a bluish green color of low value and medium chroma. The Munsell[29] designation for this color is 5.0 BG 3/5. Thinner crystals had a somewhat higher value and chroma, but pulverizing lowered the chroma while increasing the value so as to cause the material to appear almost light gray. A product contaminated with only 1% chromium(II,III) fluoride, as determined by observation with a microscope, was noticeably greener than pure CrF_2.

The melting point of CrF_2, previously reported to be about 1100°,[3,7,21] was found by thermal analysis to be $894 \pm 6°$. This was confirmed by the value $887 \pm 4°$ obtained by a thermal gradient quench.

The density of CrF_2, determined with a pycnometer at 25°, was 3.79 g./cc., which is in reasonable agreement with the 3.85 g./cc. calculated from the crystal data of Jack and Maitland.[9] Poulenc's value of 4.11 g./cc. is apparently too high.

Measurements of a CrF_2 ingot provided sufficient information for the calculation of the density of molten CrF_2. When allowed to solidify and cool to room temperature in a cylindrical crucible, CrF_2 formed an ingot having a torroidal-shaped internal void but no noticeable distortion of the outer surface. If this void is assumed to be due only to contraction on freezing and the small change in volume on further cooling is neglected, the total volume of the ingot including void represents the volume of molten CrF_2 at its freezing point. Such an ingot weighing 736 g. had a total volume of 216 cc., therefore the density is 3.40 g./cc. at 894°.

Chromium(II) fluoride, especially if crystallized from a melt, was so inert as to be difficult to attack for chemical analysis. A sodium peroxide fusion and treatment with perchloric acid was necessary in order to put the sample into solution for the determination of chromium. For the determination of fluoride by pyrohydrolysis[30] a considerably higher temperature (1050–1100°) than usual (900–950°) was required.

Chromium(II,III) Fluoride

Chromium(II,III) fluoride, found sometimes as a contaminant in CrF_2, was synthesized and characterized. A sample of the pure compound was obtained by selecting a suitable portion of the product of the partial hydrogen reduction of CrF_3. Similar to CrF_2, the compound was so inert as to be difficult to analyze. Analysis of this material indicated the composition $CrF_{2.4}$. It was more conveniently synthesized by combining at 800–900° an intimate mixture of CrF_3 and CrF_2 sealed in a platinum tube.

Chromium(II,III) fluoride also has been made by oxidizing CrF_2 with molten SnF_2. It has been found in the products of hydrofluorination of $CrCl_2$, CrF_2, and chromium metal, also in CrF_2 preparations resulting from incomplete disproportionation of CrF_3 or pyrolysis of $(NH_4)_3CrF_6$.

Phase Studies

Liquid–solid relationships were determined by examining the products of thermal gradient quenching[31] of CrF_2–CrF_3 mixtures. These products were studied principally with a polarizing microscope, but also by X-ray diffraction analysis. These quench experiments were initiated with the CrF_2–CrF_3 mixtures in platinum tubes 0.318 cm. o.d. × 0.025 cm. wall, but, as these tubes sometimes did not withstand the pressures developed at the high temperatures used to anneal the mixtures, 0.254 cm. o.d. tubes with 0.041 cm. walls were used to complete the series of experiments. The resulting data (Table I) were used to plot a phase diagram (Fig. 1).

For compositions up to 10 mole % CrF_3, the quench results were verified by cooling curve data from samples in sealed nickel capsules. At higher CrF_3 concentrations, however, the container was seriously corroded and erratic thermal data were obtained which were not used to plot the phase diagram. Much nickel metal was removed from the wall of the container and precipitated in the melt by a reaction with CrF_3 which occurred at the elevated temperature but reversed on cooling

$$2CrF_3 + Ni \rightleftharpoons NiF_2 + 2CrF_2$$

Elimination of oxygen from the chromium fluorides was important for these studies. At room temperature the chromium fluorides adsorb quantities of oxygen from the air, which react at the

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(29) A. H. Munsell, "Munsell Book of Color," Munsell Color Co., Baltimore, Md., standard edition, 1929.

(30) C. D. Susano, J. C. White, and J. E. Lee, U. S. Atomic Energy Comm. ORNL-1744, 1954.

(31) H. A. Friedman, *J. Am. Ceram. Soc.*, **42**, 284 (1959).

TABLE I

DATA OBTAINED FROM CrF_2–CrF_3 MIXTURES

Composition (mole %)		Phase change temp., °C.	Phases found just above temp.	Phases found just below temp.	Interpretation
CrF_2	CrF_3				
100	0	887 ± 4	Liquid	CrF_2	M.p. of CrF_2 from quench data
		894 ± 6[a]	...		M.p. of CrF_2 from cooling curve data
99	1	850 ± 3	Liquid and CrF_2ss	CrF_2ss	Limit of CrF_2ss at 850°
95	5	857 ± 4	Liquid	Liquid + CrF_2ss	Liquidus
		828 ± 4	Liquid + CrF_2ss	CrF_2ss + Cr(II,III) fluoride	Solidus
		850 ± 10[a]	...	...	Liquidus
		820 ± 10[a]	...	...	Solidus
90	10	841 ± 4	Liquid	CrF_2ss + Cr(II,III) fluoride	Liquidus and solidus
		840 ± 10[a]	...	...	Liquidus
		825 ± 10[a]	...	...	Solidus
85	15	835 ± 4	Liquid	CrF_2ss + Cr(II,III) fluoride	Liquidus and solidus
80	20	891 ± 4	Liquid	Liquid + Cr(II,III) fluoride	Liquidus
		822 ± 12	Liquid + Cr(II,III) fluoride	CrF_2ss + Cr(II,III) fluoride	Solidus
75	25	945 ± 4	Liquid	Liquid + Cr(II,III) fluoride	Liquidus
		826 ± 3	Liquid + Cr(II,III) fluoride	CrF_2ss + Cr(II,III) fluoride	Solidus
70	30	1022 ± 5	Liquid	Liquid + CrF_3ss	Liquidus
		998 ± 6	Liquid + CrF_2ss	Liquid + Cr(II,III) fluoride	Incongruent m.p. of Cr(II, III) fluoride
		826 ± 5	Liquid + Cr(II,III) fluoride	CrF_2ss + Cr(II,III) fluoride	Solidus
65	35	1071 ± 4	Liquid	Liquid + CrF_3ss	Liquidus
		998 ± 5	Liquid + CrF_3ss	Liquid + Cr(II,III) fluoride	Incongruent m.p. of Cr(II, III) fluoride
62	38	829 ± 5	Liquid + Cr(II,III) fluoride	CrF_2ss + Cr(II,III) fluoride	Solidus
60	40	1142 ± 4	Liquid	Liquid + CrF_3ss	Liquidus
		999 ± 5	Liquid + CrF_3ss	Liquid + Cr(II,III) fluoride	Incongruent m.p. of Cr(II, III) fluoride
		848 ± 4	Liquid + Cr(II,III) fluoride	Cr(II,III) fluoride	Limit of Cr(II,III) fluoride ss at 848°
58	42	988 ± 4	Liquid + CrF_2ss	Liquid + Cr(II,III) fluoride	Incongruent m.p. of Cr(II, III) fluoride
		930 ± 3	Liquidus + Cr(II,III) fluoride	Cr(II,III) fluoride	Limit of Cr(II,III) fluoride ss at 930°
		775 ± 14	Cr(II,III) fluoride	CrF_2ss + Cr(II,III) fluoride	Limit of Cr(II,III) fluoride ss at 775°
55	45	990 ± 4	Liquid + CrF_3ss	CrF_3ss + Cr(II,III) fluoride	Incongruent m.p. of Cr(II, III) fluoride
		980 ± 6	CrF_3ss + Cr(II,III) fluoride	Cr(II,III) fluoride	Limit of Cr(II,III) fluoride ss at 980°
54	46	997 ± 3	Liquid + CrF_3ss	CrF_3ss + Cr(II,III) fluoride	Incongruent m.p. of Cr(II, III) fluoride
50	50	1000 ± 4	Liquid + CrF_3ss	CrF_3ss + Cr(II,III) fluoride	Solidus
20	80	979 ± 6	Liquid + CrF_3ss	CrF_3ss + Cr(II,III) fluoride	Solidus
10	90	1031 ± 4	Liquid + CrF_3ss	CrF_3ss	Limit of CrF_3ss at 1031°
0		962 ± 5	CrF_3ss	CrF_3ss + Cr(II,III) fluoride	Limit of CrF_3ss at 962°
0	100	1404 ± 20	Liquid	CrF_3	M.p. of CrF_3

[a] Thermal breaks.

elevated temperatures of the experiments to form oxide and change the composition of the mixture

$$12CrF_2 + 3O_2 \longrightarrow 2Cr_2O_3 + 8CrF_3$$

Opaque in oils of low refractive index, Cr_2O_3 interferred with the examination of chromium fluorides under the microscope. Contamination of the samples was avoided by loading the tubes in a glove box that first was evacuated to less than 50 μ to remove adsorbed gases and then filled with helium purified by passage through activated charcoal cooled by liquid nitrogen.

In order to determine the melting point of

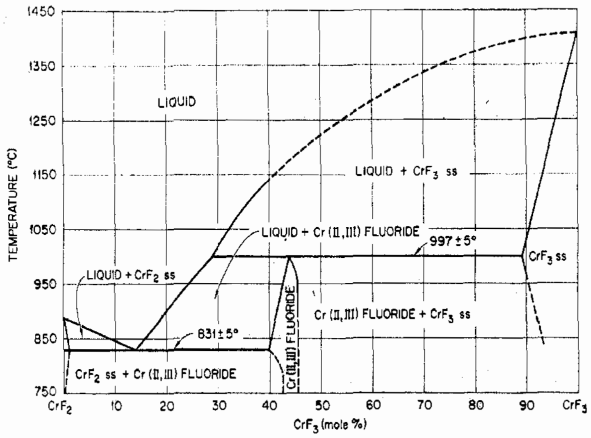

Fig. 1.—The system CrF_2–CrF_3.

CrF_2 it was necessary to prevent disproportionation into CrF_3 and volatile CrF_5 at high temperatures. This was done by sealing CrF_3 in platinum tubes. These tubes were heated to various temperatures, and the cooled products examined for evidence of melting. Samples heated to 1419° showed evidence of melting, but those heated to 1388° did not, accordingly the melting point was represented as 1404 ± 20°. Analysis of the cooled melt showed that it was not contaminated by disproportionation.

The system contains two invariant points, the eutectic at 14 mole % CrF_3 and the peritectic at 29 mole % CrF_3. The temperature of the eutectic near 14 mole % CrF_3 was established at 831 ± 5° from an average of 6 quenches at 5, 10, 15, 25, 30, and 38 mole % CrF_3.

In the system there is a single intermediate compound, chromium(II,III) fluoride, which, according to the results of quenches at 38, 40, 42, 45, and 46 mole % CrF_3, gives rise to a single phase in the composition region $CrF_{2.40}$ to $CrF_{2.45}$. The incongruent melting point of chromium(II, III) fluoride was established at 997 ± 5° from an average of data from a series of six quenches containing 30, 35, 40, 45, 46, and 50 mole % CrF_3. The composition of the compound at that temperature was found to be $CrF_{2.44}$.

Chromium(II) fluoride formed a solid solution containing about 1 mole % CrF_3, but this did not change the refractive index significantly.

A quench of the composition 90% CrF_3 + 10% CrF_2 was found to be near the edge of the CrF_3 solid solution region. The solid solution could be distinguished from pure CrF_3 by refractive index. Neither the hypothetical high temperature cubic form[32] nor any other allotropic modification of CrF_3 was observed in quenches up to 1192°.

Physical properties of the pure solid phases in the CrF_2–CrF_3 system, determined in the course of these studies, are listed in Table II. The powder pattern of chromium(II,III) fluoride, determined with CuKα radiation, includes the four strongest lines at 3.76, 3.36, 3.21, and 3.08 Å. (X-Ray diffraction data for CrF_2 and CrF_3 have been reported previously.[32–34])

Discussion

In spite of the disproportionation of CrF_3 and other problems the phase relationships in the CrF_2–CrF_3 system have been determined. Although a significant pressure of CrF_5 is present in equilibrium with CrF_3 and CrF_2 at high temperatures, the CrF_2–CrF_3 system can be regarded as condensed because disproportionation can be avoided at the relatively moderate pressures, insufficient to measurably alter a normal melting point, obtained when confining CrF_3 in platinum. A single-crystal study has been initiated at this Laboratory by J. H. Burns to determine the structure of the intermediate compound, chromium(II,III) fluoride. Chromium(III) fluoride melts at nearly the same temperature as does VF_3 (m.p. 1406 ± 15°).[35] The previously reported[21] low value of 1100° for the melting point of CrF_3 presumably was caused by contamination with CrF_2 formed by disproportionation.

The classical procedures for preparing CrF_2 all tend to form mixed products. Because of oxidation by HF, hydrofluorinations yield products containing much trivalent chromium, as either CrF_3 or chromium(II,III) fluoride. Hydrogenation of CrF_3 is useful for preparing CrF_3, but the product usually requires recrystallization and mechanical separation to remove chromium metal resulting from excess reduction. New procedures useful for preparing small batches of CrF_2 are (1) reacting CrF_3 with chromium and (2) thermal decomposition of CrF_3 and its precursor $(NH_4)_3CrF_6$. A procedure that is readily applied to prepare the needed quantities is the oxidation of chromium metal by fluorides of less active metals.

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[32] K. Knox, *Acta Cryst.*, **13**, 507 (1960).

[33] H. Insley, T. N. McVay, R. E. Thoma, and G. D. White, "Optical Properties and X-Ray Diffraction Data for Some Inorganic Fluoride and Chloride Compounds," U. S. Atomic Energy Comm. ORNL-2192, Nov. 8, 1956.

[34] American Society for Testing Materials, Chromium(III) Fluoride, X-Ray Diffraction Data Card No. 10-85.

[35] B. J. Sturm and C. W. Sheridan, "Vanadium Trifluoride," *Inorg. Syn.*, to be published.

Table II

Physical Properties of Fluorides of Chromium

	CrF_2	$CrF_{2.40}$ (Cpd. ss Limit)	$CrF_{2.45}$ (Cpd. ss limit)	$CrF_{2.9}$ (CrF_3 ss with CrF_2)	CrF_3
Density (g./cc. at 25°)					
Calculated	3.85				3.65
Determined	3.79	3.64			3.59
Color	Blue-green	Green	Green	Yellow-green	Yellow-green
Munsell	5.0 BG 3/5	10GY 5.5/4.5			6GY 7.5/4
Optical properties	Biaxial (+)[a]	Biaxial (−)[b]	Biaxial (−)	Uniaxial (+)	Uniaxial (+)[b]
	Monoclinic				
	$2V = 10°$	$2V = 55°$			
Refractive indices	$N_\alpha = 1.511$	$N_\alpha = 1.518$	$N_\alpha = 1.518$	$N_\omega = 1.562$	$N_\omega = 1.568$
	$N_\gamma = 1.525$	$N_\gamma = 1.534$	$N_\gamma = 1.537$	$N_\epsilon = 1.574$	$N_\epsilon = 1.582$

[a] H. Insley, T. N. McVay, R. E. Thoma, and G. D. White, U. S. Atomic Energy Commission Report ORNL-2192, Nov. 8, 1956. [b] C. F. Weaver, Oak Ridge National Laboratory, private communication, 1961.

The bluish green color of Poulenc's product indicates that he obtained reasonably pure CrF_2. Although his product of hydrofluorination would be expected to contain much trivalent chromium, his fusion to "recrystallize" apparently converted this into CrF_2 by disproportionation. Similarly, disproportionation at high temperatures serves to explain why Muetterties and Castle[10] obtained CrF_2 at 900°, but CrF_3 at 300° in their treatment of chromium metal with HF gas. The disproportionation of CrF_3 into CrF_2 and CrF_5 at high temperatures was not anticipated by Brewer,[36] who, in his estimate of thermodynamic properties, regarded CrF_3 to be stable to even above its boiling point.

In the instability of the divalent state in the presence of HF, chromium is similar to vanadium, the dichloride of which is readily converted to VF_3.[37] A similar element, iron, on the other hand, has a more stable divalent state, as $FeCl_2$ can be given a prolonged hydrofluorination to form FeF_2 containing no detectable FeF_3.

The CrF_2 synthesized at this Laboratory was used primarily for corrosion studies of chromium alloys considered as containers for molten reactor fuels. For these studies it was very important that the CrF_2 should not be significantly contaminated with other alloy constituents (*e.g.*, Ni and Fe) or chromium in a valence state other than chromous. Also contamination with opaque material (*e.g.*, Cr^0, CrN, and Cr_2O_3) was to be minimized to avoid interference with optical evaluation of the CrF_2 or products resulting from its use in experiments. Chromium(II) fluoride, made by the reaction of SnF_2 with chromium, was especially desirable. It was generally lower in total impurities than were the products of other procedures. More important, those impurities present (principally 0.1–0.2% Sn) did not interfere with the experiments for which the CrF_2 was used. Chromium(II) fluoride, so prepared, was used by Cable, Wilkinson, and Wollan[38] for neutron diffraction studies.

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