

[CONTRIBUTION FROM THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY]

Pure Chromyl Fluoride¹

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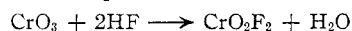
Pure chromyl fluoride was isolated for the first time by means of a vacuum apparatus built out of copper, silica-free glass and Kel-F tubing. The violet-red crystals reach a pressure of 760 mm. at 29.6° and melt to an orange-red liquid at 31.6°; the vapor pressure at the triple point equals 885 mm. The compound was prepared from CrO₃ and anhydrous hydrogen fluoride; its solubility in HF is very low at -78°. The purification made use of the fact that it forms stable, non-volatile triple addition compounds with HF and KF (or NaF). The fluoride is extremely reactive, particularly with any type of oxidizable organic compound.

The fluorine analog of the well known chromyl chloride has not been isolated in the pure form heretofore. The literature on chromyl fluoride is full of conflicting and sketchy information, which necessitates some discussion. The elusive vapors of a red chromium fluorine compound were observed² 125 years ago upon heating a mixture of fluorspar, chromates and sulfuric acid. For a long time it was considered to be CrF₆, for example, by Mendelejeff,³ although some chemists⁴ assumed the formula CrO₂F₂ as an analog of CrO₂Cl₂. Ruff⁵ in an unsuccessful attempt to isolate the compound concluded that "All speculations up to the present regarding the composition of the red gas lack any analytical basis." More recent German attempts were at best only partly successful. Fredenhagen^{6,7} observed that, when using really anhydrous HF, Gore's reaction,⁸ *i.e.*, between alkali chromates and HF, led to the evolution of a red-brown, easily condensable gas, which was considered to be CrO₂F₂, although an isolation was not attempted. v. Wartenberg⁹ succeeded in isolating impure CrO₂F₂ by treating CrO₂Cl₂ with elementary fluorine and stated that the fluorine atoms are attached so loosely to the chromium as to make the compound a strong fluorinating agent, a conclusion which is obviously incorrect. His product was evidently contaminated with free fluorine (since it also reacted with water to form ozone) and other impurities causing polymerization, and he estimated the boiling point "in view of partial polymerization, unpreparable liquid" to be 80°. Wiechert,¹⁰ in the most recent attempt, treated liquid anhydrous hydrogen fluoride in a quartz flask with dichromate and obtained the compound as a liquid at -40°, evidently contaminated with hydrogen fluoride and perhaps some silicon tetrafluoride. At 0° it was completely vaporized to a gas.

Since chromyl fluoride is extremely reactive with glass and even quartz, it was necessary in the past to work in a metal system. Our success in isolating the pure compound was due primarily to the

availability of traps and tubing of silica-free glass¹¹ and inert, transparent plastics such as Kel-F, which permitted *visual* observation of the reaction products without contaminating them.

Chromium trioxide reacted readily with anhydrous hydrogen fluoride forming chromyl fluoride according to the equation



This reaction is reversible, and water will easily hydrolyze the fluoride back to CrO₃. The gaseous fluoride will hydrolyze instantly by water vapor to a very characteristic smoke-like pink powder. We found, however, that by using a large excess of HF, *i.e.*, over 10 moles of HF per mole of CrO₃, good yields (85% and higher) of chromyl fluoride can be obtained (see Experimental part).

Pure CrO₂F₂, at room temperature, forms either deep violet-red large and well developed rhombohedral-like crystals, an orange-red liquid, paler in color than CrO₂Cl₂, or a red-brown gas. The crystals sublime readily and reach a pressure of 760 mm. at 29.6°. They melt at 31.6°, and the vapor pressure at the triple point is 885 mm. The vapor pressure curves of both solid and liquid are shown in Fig. 1.

The vapor pressure of the solid can be expressed by the equation

$$\log_{10} p_{\text{mm.}} = 6.25189 + 959 \times \frac{1}{T} - 599333 \times \frac{1}{T^2} \quad (1)$$

The heat of sublimation, from the above equation, is equal to 13,800 cal./mole.

The vapor pressure equation for liquid CrO₂F₂, determined only over a narrow range, is given by the equation

$$\log_{10} p_{\text{mm.}} = 8.80494 - 1785.5 \times \frac{1}{T} \quad (2)$$

The heat of vaporization at the triple point is calculated from equation (2) to be 8200 cal./mole. The heat of fusion, *i.e.*, the difference between the heat of sublimation and vaporization, equals 5600 cal./mole.

The fluoride crystallized nicely from anhydrous HF on cooling. It was soluble only to a small extent at -78° and at that temperature the saturated solution was only slightly colored. It was appreciably soluble at room temperature and gave a red solution.

The pure fluoride showed no sign of polymeriza-

(1) Presented before the XIIth International Congress of Pure and Applied Chemistry, New York City, September 10-13, 1951. See Abstracts of Papers, p. 525.

(2) Unverdorben, *Annalen Min.*, [2] **1**, 135 (1827).

(3) D. I. Mendelejeff, "Principles of Chemistry," German Edition, St. Petersburg, 1892, p. 959.

(4) See Olivieri, *Gazz. chim. ital.*, **16**, 218 (1886).

(5) O. Ruff, *Ber.*, **47**, 658 (1914); see also his book "Die Chemie des Fluors," Berlin, 1920, p. 115.

(6) K. Fredenhagen, *Z. Elektrochem.*, **37**, 684 (1931).

(7) K. Fredenhagen, *Z. anorg. allgem. Chem.*, **242**, 23 (1939).

(8) Gore, *J. Chem. Soc.*, **22**, 395 (1869).

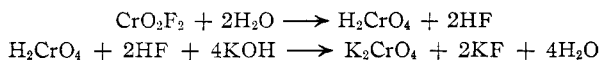
(9) H. v. Wartenberg, *Z. anorg. allgem. Chem.*, **247**, 135 (1941).

(10) K. Wiechert, *ibid.*, **261**, 315 (1950).

(11) Aristid V. Grosse, "Note on the Use of Silica-Free Glasses for Handling Anhydrous Hydrogen Fluoride and Uranium Hexafluoride," MDDC-1040 (Manhattan District Document Copy) Dept. of Physics, Columbia University. Date of manuscript: Sept. 1945; date declassified: June 13, 1947.

tion when stored in darkness for a period of many months in a sealed aluminum phosphate glass tube or in a Kel-F tube. It polymerized very slowly to a solid polymer, first observed by von Wartenberg,⁹ under the influence of daylight or ultraviolet light. It was stable at room temperature in the dark for an indefinite period in contrast to CrO_2Cl_2 , which has a tendency to oxidize to free chlorine coupled with a reduction to solid mixed chromic chromates.

It can be titrated, after hydrolyzing in water with standard alkali, using phenolphthalein as an indicator, in line with the over-all equations



The purity of our preparation was 99.5% of theory, based on above equations. The chromium content was determined iodometrically, after hydrolysis, by quantitatively reducing chromic acid to trivalent chromium. (*Anal.* Calcd. for CrO_2F_2 : Cr, 42.63. Found: Cr, 42.38, 42.38.) The gas is monomolecular, for the molecular weight was found to equal 121.4 at 25° and 500 mm. (theory for CrO_2F_2 , 122.0).

Chromyl fluoride is extremely reactive, particularly with any type of oxidizable organic compound. At elevated temperatures, paraffin gases such as methane or butane ignite in the gas and burn with a bright flame producing a smoke of Cr_2O_3 and CrF_3 . Pure CrO_2F_2 does not combine with KF or NaF at room temperature. Potassium bifluoride, $\text{KF}\cdot\text{HF}$, reacts readily at room temperature with chromyl fluoride forming the interesting triple addition compound $\text{KF}\cdot\text{HF}\cdot\text{CrO}_2\text{F}_2$. In this respect it is analogous to UF_6 which forms similar compounds.¹²

Experimental

Apparatus.—A standard type vacuum apparatus was used which contained no parts made of silica glass. The main train consisted of copper tubing, with copper reaction vessels and traps. They were connected with standard refrigeration industry flare fittings. A number of traps and tubes consisted of Kel-F tubing, while aluminum phosphate¹³ glass was used in some parts.

The vapor pressure was measured in an isoteniscope constructed of copper. The U-tube consisted of Kel-F tubing, and was filled with either Kel-F tube oil or mercury, or both.

Preparation of Raw Chromyl Fluoride.—A 250-g. (2.5 mole) sample of Baker Analyzed Grade CrO_3 was placed in a round copper flask, the latter cooled, and 600–700 g. (30–35 moles) of anhydrous hydrogen fluoride (Harshaw Chemical Co., 99% pure) condensed in the flask. The mixture was warmed up to room temperature and allowed to stand, with occasional shaking, for a few hours. The flask was then cooled to -78° and the acid layer (approximately 93% HF, 7% H_2O) decanted. The quantity of dissolved chromyl fluoride was only 5–10 g. (It is important to use the large excess of HF indicated; otherwise ice, or ice + HF, separates from the acid phase in this stage.)

After decantation the copper reaction vessel was closed, the residue allowed to warm up again to above the melting point of chromyl fluoride and cooled a second time with Dry Ice. Thus, a solid bottom layer of chromyl fluoride was obtained, which contained only a little HF. The top layer

(12) A. V. Grosse, "A Method for Handling and Purifying UF_6 in Glass Vessels by Means of Alkali Fluoride Getters," presented before the Fluorine Symposium of Ind. & Eng. Div., A.C.S., Sept. 15–19, 1947. See Abstracts pp. 26 and 27. Available as MDDC-1038 (Manhattan District Document Copy) from Technical Information Division, U.S. Atomic Energy Commission, Oak Ridge, Tennessee.

(13) Manufactured under patents of the American Optical Company, Southbridge, Mass.

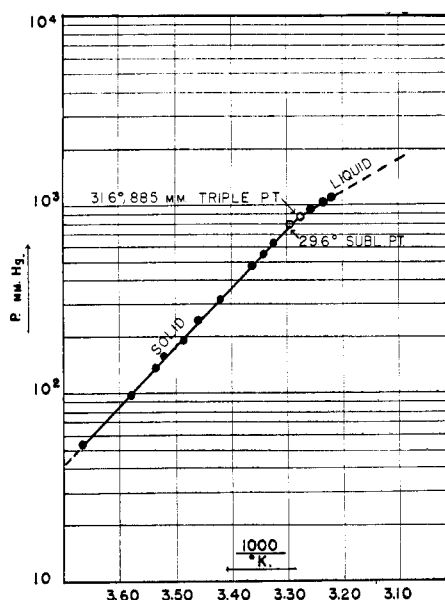


Fig. 1.—Vapor pressure of CrO_2F_2 .

of HF, containing a little water, was decanted a second time. Part of the product was then distilled *in vacuo* into a transparent Kel-F reaction vessel. Here a further separation of HF from chromyl fluoride was accomplished since HF distilled over first. Liquid HF cooled to -78° can be decanted simply from the small amounts of chromyl fluoride distilling with it.

Purification of Chromyl Fluoride.—The separation of the last traces of HF and water and production of a chemically pure chromyl fluoride was an important next step. If this step is not carried out properly an unstable product is formed. If carried out correctly, chromyl fluoride is obtained which can be kept indefinitely or at least for many months without change in its properties, particularly without polymerization. Advantage was taken of a method originally used for the purification of the chemically similar uranium hexafluoride.¹² This method is based on the formation of the triple addition compound, $\text{K}(\text{Na})\text{F}\cdot\text{HF}\cdot\text{CrO}_2\text{F}_2$, described below.

If one distills the impure chromyl fluoride through a tube containing sodium fluoride or potassium fluoride, any residual hydrogen fluoride (or water) in it is converted into solid triple compounds, combining with a corresponding amount of chromyl fluoride. However, and this is the main point, the *uncombined* chromyl fluoride is very pure. The total amount of combined chromyl fluoride is about 5% of the total amount formed.

There are many ways in which this purification can be carried out. It is preferred to compress dry NaF or KF into standard size pills. These are put into a 100- or 200-cc. flared copper, or, more advantageously, Kel-F tube, and connected to the reaction vessel by means of standard refrigeration fittings. The vapors of CrO_2F_2 are passed through this tube at atmospheric or slightly superatmospheric pressure at a slow rate (for a period of 2 to 4 hours or conveniently overnight) and condensed in a copper or Kel-F trap. This step may be repeated a second time if a particularly pure preparation is desired, or some solid NaF or KF pills may be placed into the preparation tube to serve as getters.

The pure preparation should be distributed into several copper and/or Kel-F tubes and kept in the dark to avoid polymerization. (After all the volatile chromyl fluoride is distilled out of the copper flask, there remains as a residue a viscous dark brown material which contains some chromium, oxygen and fluorine, and which corresponds in quantity to about 5% of the chromyl fluoride formed.)

The total yield of chromyl fluoride is about 85% of the theoretical (*ca.* 260 g.) and can be made higher by being particularly meticulous in separating the hydrogen fluoride by physical means.

The Reaction of Chromyl Fluoride with Potassium Bifluoride.—The system of potassium bifluoride and chromyl

fluoride was studied in the following manner. A small copper reaction vessel with a Hoke valve was provided, maintained at constant temperature, and aliquot amounts of the gas phase were pumped off at various intervals, the total pressure of the system and the loss in weight of the reaction vessel being determined. The temperature was kept constant at 15.0°. The over-all results obtained are shown in Fig. 2.

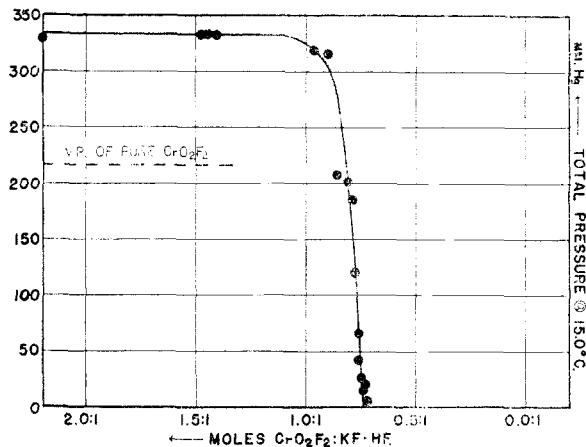


Fig. 2.—System $\text{CrO}_2\text{F}_2 + \text{KF}, \text{HF}$ at 15.0°.

The HF content of the potassium bifluoride was determined by alkali titration of a sample; it proved to be 97%

KHF_2 . Chromyl fluoride was condensed over this pure bifluoride in a molar ratio $2.2\text{CrO}_2\text{F}_2:1\text{KHF}_2$. In the initial part of the curve the vapor pressure was appreciably above the vapor pressure of pure chromyl fluoride, indicating that a more volatile constituent was being pumped off simultaneously with the chromyl fluoride. This volatile constituent proved to be hydrogen fluoride. This quantity corresponded to a decrease of about 0.2 to 0.25 mole of hydrogen fluoride per mole of the original KHF_2 as determined by titration. The pressure of the system decreased rapidly at a molar ratio of about 1:1 to about 0.8:1 and reached a value of below 4 mm. at 0.75:1. The composition of the yellow residue was determined by titrating the chromyl fluoride iodometrically and the total acidity by titration with alkali. The ratio $\text{CrO}_2\text{F}_2:\text{HF} = 1:0.97$. Thus the final mixture contained the compound $\text{KF}\cdot\text{HF}\cdot\text{CrO}_2\text{F}_2$ and about 20 mole % of KF due to loss of HF indicated above.

Analysis of CrO_2F_2 .—The following procedure was found convenient. The sample was sublimed into a dry and fresh Kel-F tube, the tube sealed by means of hot tongs ($\approx 200^\circ$), and weighed. All the chromyl fluoride was then sublimed into one end of the tube by cooling in Dry Ice and the other end cut off with a razor blade and the sample tube quickly inserted into a glass stoppered erlenmeyer flask containing an excess of standard alkali. After complete hydrolysis had taken place, *i.e.*, when all the red crystals had disappeared, forming a pale yellow solution of chromic acid, the Kel-F tube was thoroughly rinsed out with distilled water, all washings added to the hydrolysate, diluted to a desired volume and titrated in the usual manner. The Kel-F tube was dried and weighed with the tip, thus giving the weight of the sample by difference.

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A Study of the Solubility Limits at 35° in the System NaBr—NaCl

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A study of the ternary system sodium bromide–sodium chloride–6.6 molal sodium hydroxide at 35° shows that the two salts form a continuous series of solid solutions with no miscibility gap. This experimental result is in disagreement with the calculations of Fineman and Wallace and of Hovi and Hyvönen which indicate limited miscibility below 50° in the binary system sodium bromide–sodium chloride.

Recent thermodynamic and statistical calculations by Fineman and Wallace² and by Hovi and Hyvönen³ have indicated limited miscibility below 50° in the binary system sodium bromide–sodium chloride. The former investigators report an upper consolute point at 341°K. and 0.45 mole fraction of sodium bromide, while the latter estimate a critical solution temperature of 323°K. Both estimates are based upon the nature of the free energy *vs.* composition isotherms for the system. To establish experimentally the existence of any miscibility limits in this system below the reported critical solution temperatures, a study has been made of the ternary system sodium bromide–sodium chloride–6.6 molal sodium hydroxide at 35°. An examination of the phases present at equilibrium in this system showed the absence of any solid phase solubility limits.

Experimental

Choice of Solvent.—Water, the most convenient solvent for a study of this kind, could not be used because below

50.2° sodium bromide crystallizes from water as the dihydrate. Some solubility measurements were carried out in absolute methanol,⁴ but the rate of attainment of equilibrium in the solid phase was prohibitively slow. X-Ray examination⁵ of the solids present after the pure salts had been agitated for several months in contact with methanol showed, in most cases, the presence of two phases, one a bromide-rich solid solution and the other pure sodium chloride. These results are in qualitative agreement with the observations of Matsen and Beach,⁶ who found that at elevated temperatures in the binary system the solution process occurs by the incorporation of chloride ions into the sodium bromide lattice and not *vice versa*.

Solubility data of Nikolajew and Rawitch⁷ show that sodium bromide crystallizes in the anhydrous condition at room temperature from concentrated sodium hydroxide solutions. These data and those of Schreinemakers⁸ for sodium chloride indicate that at 35° the solubilities of

(4) Measurements made by Dr. S. E. Blum, formerly of this Laboratory.

(5) We are indebted to Dr. S. Weissman and the late Dr. A. J. Reis of the Engineering Experiment Station, Rutgers University, for their assistance in the X-ray examination of the solids crystallized from methanol.

(6) F. A. Matsen and J. Y. Beach, *THIS JOURNAL*, **63**, 3470 (1941).

(1) General Electric Research Laboratory, Schenectady, N. Y.
(2) M. A. Fineman and W. E. Wallace, *THIS JOURNAL*, **70**, 4165 (1948).

(3) V. Hovi and L. Hyvönen, *Ann. Acad. Sci. Fennica, Math.-Phys. Ser. A*, 106 (1951).

(7) V. I. Nikolajew and M. I. Rawitch, *Zhur. Obs. Khim.*, **1**, 789 (1931), reported in Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1940, p. 1156.

(8) F. A. H. Schreinemakers, *Z. physik. Chem.*, **68**, 83 (1910).