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Source: Zeitschrift für anorganische und allgemeine Chemie, Vol. 217, No. 1,
Feb. 1934.

Zeitschrift für anorganische
und allgemeine Chemie
Vol 217, No 1
23 February 1934

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PRODUCTS OF REACTION OF THE VARIOUS FORMS OF CARBON
WITH FLUORINE II (CARBON-MONOFLUORIDE)

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(with 4 figures in the text).

Combustion of different forms of carbon in fluorine yields different mixtures of carbon fluorides. (O. Ruff and R. Keim, Z. anorg. u. allg. Chem., Vol. 192, p. 249, 1930). Our first task was a somewhat more detailed analysis of the composition of such mixtures, showing how the composition depended upon the conditions of the experiment. The other task was to trace the causes of the violent explosions observed whenever the carbon did not catch fire in the fluorine current because this current offered an inadequate supply of heat, but rather absorbed fluorine, and thus build^d up a new supply of heat. The explosions are analogous to those occasionally observed when oxygen-containing activated carbon is heated, a process, by the way, which has been responsible for a lot of trouble.

Results from our investigations are as follows: ordinary norite, that is to say norite containing oxygen, or air and water, (the form of carbon having the lowest degree of crystalline order), readily catches fire in fluorine, for instance when contained in a copper tube, and changes into a mixture of various fluorides. But a smaller or larger residue of a more or less pure "car-

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carbon monofluoride" CF (to be eliminated below) is left behind. Norite free from oxygen, that is to say norite, degassed in a high vacuum at about 1000 degrees Centigrade for two hours, can be heated in fluorine under a pressure of about 25 millimeters up to 280 degrees without being ignited, but nevertheless combining with fluorine. The combination with fluorine continues at 280 degrees until the CF composition has been reached. If norite is spread along the interior of a copper tube and the tube heated from the outside to about 400 degrees, the norite at the side where fluorine is admitted will catch fire, ~~to be sure~~, but the portions in the rear ~~of the fluorine~~ (purified by the products of reaction) ~~have CF~~ ^{norite} as soon as the concentrated gas reaches and the unconverted is ignited, the CF is explosively decomposed. ~~Violent explosions take place~~ at definite intervals.

Combustion follows a regular and smooth course only above about 540°C.

Graphite does not ignite at all in fluorine at ordinary temperatures; it combines with and absorbs only a small amount, but can be converted into CF at about 420°. Violent explosions occur periodically at about 500° under conditions similar to those observed with norite, but these explosions disappear as temperatures increase. Fluorination is uniform and free from danger at about 700° in this case as well. (See Section A).

The nature and amount of volatile fluoride created by combustion of norite and graphite in fluorine depend not so much on the crystalline order of the two carbon varieties as on the conditions under which fluorination takes place. Higher temperatures and higher fluorine concentrations favor the formation of low molecular fluorides, especially of CF_4 ; lower temperatures and fluorine concentrations result in higher molecular fluorides up to at least C_5F_{12} (see Section B).

We call "carbon monofluoride" the gray substance, product of reaction (composition CF), which is obtained at approximately 280° from oxygen-free norite or at approximately 420° from graphite. This substance is not wettable with water and is called, dependent on its origin, "graphitic" or "noritic" fluoride.

~~... which does not wet out~~
 with water, is called ~~as a~~ monofluoride of the graphite or graphite
~~fluoride, and is the substance~~ which is obtained,
 as an independent chemical compound, having naturally quite peculiar qual-
 ities, it is characterized by its grey color, by the constancy of compo-
 sition (see Section C.) in spite of the different natures of graphite and
 norit, and in spite of the differences in the fluorine concentrations em-
 ployed in the production. Moreover this compound has an electric con-
 ductivity 100,000 times less powerful than that of graphite (see Section
 E.) and the characteristic presence of an ionic lattice.

The thermal decomposition of monofluoride into a mixture of volatile
 fluorides and carbon (see Section D.) takes place with powerful evolution
 of heat. The composition of the gaseous mixture, as well as the nature
 of the carbon residue depends on the conditions under which the experiment
 is carried out; they permit us to draw inferences with respect to the
 course taken by the decomposition (see below).

The ^{capillary} ~~adsorption~~ ~~ability~~ of the noritic GF is considerably changed
 with respect to that of norit. Water does not wet GF. Neither GF nor
 norit takes up any HCl from alcoholic solutions. It does, how ever, take
 up NaOH and is capable of forming a brown colloidal solution with the
 latter; it has, therefore, acidic properties. Methylene blue is adsorbed
 to a slight extent only by norit and not at all by GF; both these ~~sub-~~
 substances unite with phenol ^{very} slightly ~~and~~ in equal amounts. The
~~building-in~~ ^{binding-in} of fluorine ions (see below) has not only stripped the car-
 bon atoms of ^{their} ~~an~~ "unsaturated" character ^{and has lowered the order of con-}
~~ditioning pure absorption~~ ^{ditioning pure absorption} but apparently also of the capillary structure
 which ~~is responsible for~~ ^{is responsible for} the "capillary condensation" (see Section E).

The X-ray ~~photographic~~ ^{photographic} study revealed that the crystalline ~~structure~~
~~of~~ of the graphite, as well as the low ~~degree of~~ order of norit are

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substantially retained in the CF forms. The fluorine elements are densely packed between the fairly widely spaced basal planes of the graphite (see Section F and below).

The following conclusions can be reached by studying the rate of formation and decomposition of CF, the dependence on conditions under which the experiment is conducted, the electric conductivity and the structure which can be ascertained by roentgenography.

The fluorine molecules falling on the carbon surface at room temperature are retained temporarily by van der Waals forces, that is to say, they become adsorbed; on the other hand after the decomposition of the molecules fluorine ions, insofar as they are sufficiently excited are held by normal valency forces. Rising temperatures increase the number of excited fluorine molecules; therefore, the degree of absorption recedes more and more with respect to the valence bond.

The diffusion of fluorine ~~ions~~ in the graphite lattice occurs at the most suitably available points, namely vertically to the orientable faces between the C-basal planes. The widening of the lattice required for this purpose takes place by means of thermal agitation of the basal planes against each other; the deposited fluorine ions, ~~intercalate~~ intercalate. The widening and mobility of the fluorine ions are sufficiently powerful at 400 ~~degrees~~ to make the saturation with ~~graphite~~ ~~to~~ CF possible within a relatively short time, to eliminate the metallic bonds in the graphite lattice, thereby destroying the electrical conductivity.

The final result of the diffusion of fluorine in the graphite lattice brings about two experimental findings:

- (a) The ascertained density value, $d \approx 2.39$, for the lattice saturated with fluorine, and

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(b) The X-ray spectroscopic findings, according to which the intervals of the crismatic face: $10\bar{1}0$ and $11\bar{2}0$ have not changed, while the basic reflection has disappeared. ~~These~~ ~~the~~ ~~experimental~~ data permit us to draw the following conclusions:

(1) The constant of the crismatic intervals determines the basal surface area of the CF-lattice as $\frac{2.46^2}{2} \cdot \sqrt{3} = 5.36$ square Ångströms, permitting us to calculate the increase in volume, with respect to the elementary cube of the graphite lattice we obtain a volume of 96.5 cubic Ångströms for 4 CF-molecules; 4 C-atoms have a volume of 35.6 cubic Ångströms in the graphite lattice. Thus it will be seen that the increase in volume amounts to 49.6 cubic Ångströms or to 141 per cent of the original graphite volume, that is to say, 12.5 cubic Ångströms for each fluorine unit. If we compare with this number the space requirement in the densest structure (74 per cent of space filled) of a fluorine ion having a radius of $r = 1.33$ Ångströms ($V = 9.87$ cubic Ångströms) and $\frac{9.87}{0.74} = 13.3$ cubic Ångströms, it will be found that both numbers lie within the same order of magnitude, warranting the conclusion that the fluorine molecule has become split into fluorine ions upon combining with carbon.

(2) The increase in volume furthermore enables us to ascertain that the interval between two carbon basal surfaces has been widened from the original 3.4 Ångströms to 3.17 Ångströms.

(3) Hence to the prismatic surface interval which has remained unchanged, we are in a position to calculate the amount required for widening the fluorine ions (in the case of suitable building in of such fluorine ions between the carbon surfaces) in order to also provide the incorporation of one carbon-bearing fluorine unit for each C-unit. The already mentioned 5.21 Angstroms (equal to the area of a carbon hexagon) equals two C-units with respect to two fluorine units in this area.

It is impossible to arrange the fluorine ions in a regular lattice along a parallel surface, in a manner similar to that of C-units, due to the fact that the fluorine ion extends beyond the limit of a hexagon. It is possible to ascertain by means of calculations that, corresponding to Figure 1, the fluorine ions must be displaced from one another by 1.01 Angstroms along the z-axis (vertically to the base); as a result, six additional carbon atoms in intervals of 1.01 Angstroms each originate between two carbon surfaces. The first of the six fluorine surfaces lies 1.46 Angstroms , the last $1.46 \text{ plus } 5 \cdot 1.01 = 6.51 \text{ Angstroms}$ beyond the carbon initial surface. The latter surface now following is analogous to the original graphite lattice, displaced parallel to the initial surface in such a manner that carbon units ($r = 0.71$) are arranged vertically over the unoccupied hexagon centers. (Figure 1, Proportional representation after F. Ebert.)

It is obvious, therefore, that an interval of $1.33 + 0.71 = 2.04 \text{ Angstroms}$ as opposed to the original value of 1.46 should have been assumed with respect to the interval between the last fluorine surface and the new carbon surface, unless (as illustrated by the symmetric bases (see Figure 1) and also plausible in accordance with the best possible

methods of space filling) a rupture in the second carbon surface occurs because the fluorine ions have been deposited in a one-sided manner. This amount may be calculated as 2.04 \AA , with the result that the interval between the last fluorine surfaces and the average value of the carbon surface amounts to $2.04 - 0.50 = 1.54 \text{ \AA}$. Thus the interval between the two carbon surfaces has been calculated as $1.26 \text{ \AA} + 5 \times 1.01 + 1.54 = 8.05 \text{ \AA}$. This value is sufficiently close to that calculated on the basis of density (8.17). In view of the fact that according to experience the density values measured are smaller than those ascertained from the structure, the insignificant difference still present is found in the direction where it was expected. The value of ≈ 2.39 pyknometrically ascertained is replaced by 2.43 calculated on the basis of the structure.

The disappearance of the basal reflection of the original graphite lattice in the x-ray picture is explained by the multiple deposit of intermediate surfaces from the fluorine ions. A reflection along the basal surfaces having an identity interval of $2 \times 8.05 = 16.1 \text{ \AA}$ escapes observation, first, because the angle of deflection is too small, which causes the reflection in the Debye-Scherrer diagram to disappear in the strong fog density around the perforation point; and, second, the number of the superimposed carbon surfaces is not large enough to produce a sufficiently sharp line of interference. Nor will the intercalated fluorine surfaces themselves produce any interference, due to the fact that their intervals with respect to the adjacent carbon surfaces are irregular and furthermore they are poorly charged in proportion to the carbon surfaces.

In heating the monofluoride to temperatures higher than about 500 degrees, the displacement of the fluorine ions within the graphite lattice becomes so brisk that, when working under a reduced pressure, they migrate

towards the periphery of the graphite lamellae. These ~~are~~ conforming closely to the requirements involving the probability of a fixed migration velocity -- the ions forcibly displace a number of carbon atoms in the form of carbon fluorides which can be carried away with the least possible expenditure of energy. Should the increase in temperature occur at a too rapid rate, the fluorine ions will no longer individually reach the periphery of the graphite lamellae, but because of the heavier accumulation in isolated places they build a closed fluoride molecule within the graphite lattice, ~~and to be sure~~ ^{the most easily volatilized} ~~the most easily volatilized~~ CF_4 saturated with fluorine, ~~will do so~~ ^{and} ~~due to lack of space~~ ^{and} along, this type of fluoride formation must result in the removal of portions of the local surfaces or in pulverizing results into dust. In a unit (in which substances like graphite crystals, if present at all, are such matter) a surface accumulation of fluorine ions cannot take place in the interior. Decomposition takes place essentially along the edges and produces accordingly fluorides of increasing carbon content.

GENERAL ASPECTS

(A) Reactivity of Graphite and Graphite with Fluorine

- (1) Graphite with 0.75 per cent ash content, having a mesh size of 200 meshes per square centimeter, was heated in a quartz tube for two hours to 1000 degrees in high vacuum before use; on cooling off in the vacuum it was stored in an exsiccator filled with air.

Manner of procedure: A weighed amount of graphite was spread out thinly in a boatshaped tray of calcinated calcium fluoride and exposed to the effect of a fluorine current of 15 cubic centimeters per minute for a definite period of time in a copper tube 35 centimeters long and 2 centimeters wide. The tube was heated from the outside and cooled at both ends. The final result was varied, depending on the outside temperature

of the heating space, as shown in the table below. The final result has been ascertained by simply weighing the fluorine amounts absorbed.

The data at 420 degrees has been collected in the diagram of Figure 2 (absorption of F_2 by Graphite. Zeit. Stdn. = time in hours). They follow an asymptotic course and reach a final value of about 56.4 percent. Since some graphite has also been decomposed in these experiments (see below), the weight accretions as used in plotting the curve represent actual values.

Table I.
FLUORINE ABSORPTION BY GRAPHITE

TEMPERATURE (DEGREES C.)	TIME	AMOUNT OF F_2 ABSORBED IN 100 GRAMS OF RE- ACTION PRODUCT	BEHAVIOR OF RE- ACTION PRODUCT
20	5 and 6 hours	About 15	No noticeable re- action by heating.
360	2 and 3 hours	About 15	No noticeable re- action by heating.
420	1 1/2; 2 1/2; 3 1/2; 4 1/2; 5 1/2; 6 1/2 hours	55.9; 56.6; 57.5; 57.9; 58.2; 58.35	Strong gas generation on heating accompanied by flame-up and soot formation.
460	After 10 minutes	Explosion; soot is blown out of the tube by gases.	

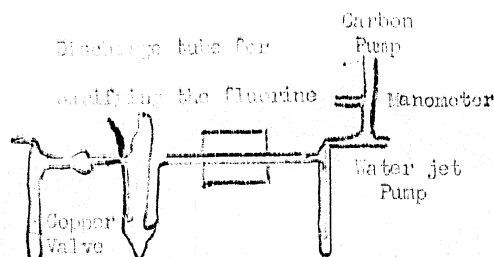
The dependence of the fluorine content on time at 420 degrees in the time interval from 1 1/2 to 6 1/2 hours corresponds to the equation $a = 10^m \frac{t + m}{k}$ ($a = \%F$ in the final product; $t =$ time of fluorization in hours; $k = -6.0205 \times 10^{24}$ and $m = -1.330$).

The diffusion resistance of equally thick layers will during this time be smaller for fluorine molecules penetrating from the outside towards the inside.

As previously pointed out, a small amount of graphite is decomposed during heating in the fluorine current as "waste." This waste first affects the oxygen containing portions along the surface, decreasing with the progress of the fluorination process. In addition to CO_2 and CO , it yields a mixture of 70-80 per cent CF_4 and 20-30 percent C_2F_6 , etc.; when fluorine and graphite are free from oxygen as possible are used, the waste contributes about 3 percent to the formation of CF_4 .

(2) The nozzle contained 1.2 percent ash, and it was hardly possible to detect any graphite interference in the X-ray picture. Prior to its use, nozzle had been heated for two hours at 1000 degrees in high vacuum; on cooling off in the vacuum it was either placed in an oxidizer filled with air, that is to say, again saturated with dry air, subsequently, or annealed in the tube of the apparatus as illustrated in Figure 3. Subsequently pure, dry nitrogen was admitted and immediately fluorinated. When experiments are carried out with vapor-containing nozzle, 14 millimeters of ~~vacuum~~ ~~pressure~~ ~~was~~ ~~imposed~~ to the nitrogen. The gaseous reaction products ~~should be~~ recaptured and analyzed in the condensing tube, whenever possible.

Figure 3



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Apparatus, see Figure 3 (made in fluorine free from O_2 , at a pressure of 25 millimeters). The apparatus as illustrated contains a "discharge tube" for the purpose of liberating the fluorine of its oxygen content (O. Luff and W. Menzel: Z. anorg. u. allg. Chem., Vol. 211, p. 204, 1933.); in experiments carried out with fluorine a pressure of 25 millimeters at 280 degrees, ~~has been employed~~. The tube was omitted in experiments carried out under higher fluorine pressure.

The crude fluorine was at first "frozen" in the first condensing tube at the left, (in the tube the lower end of which is just touching the liquefied air, small amounts of the following accumulate: CO_2 , O_2 , CO , and C_2H_2 ; SO_2 , F_2 $\Delta^{\circ}C$ in this connection O. Luff and W. Menzel, in Z. anorg. u. allg. Chem., Vol. 198, p. 49, 1931, chlorine and chlorine oxide, in addition to a still unknown but colorless gas yielding ~~an~~ ~~stance~~ [perhaps NO_2] which is decomposed at higher temperatures in the manner of chlorine oxide. The condensing tube is frequently destroyed by a strong explosion during the thawing out process and must for this reason be handled with the utmost care.) ~~which~~ ~~it~~ entered (possibly via the discharge tube) the copper heating tube ~~of~~ about 100 centimeters length and 20 millimeters diameter containing nitrite in a copper or fluorspar boatshaped tray. The thermo-~~electric~~ couple was attached to the reaction tube (insulated by means of a thin asbestos paper support from below and a thick asbestos paper layer above) in order to determine the outside temperature in the reaction chamber. Liquefied air cooled the condensing tube to the right.

TABLE OF THE INDIVIDUAL EXPERIMENTS:

DEGREES C.

- 20 (a) Air containing nitrite from the ~~oxidator~~ ^{de} immediately catches fire in the fluorine current; about 20 percent fluorine containing residue.

DEGREES C.

- 20 (b) The same applies to oxygen containing norit.
 (c) The same applies to norit free from oxygen, but containing water vapor.
 (d) The same applies to norit originally free from oxygen, which has been incompletely fluorized and again brought in contact with air.
 (e) Norit free from oxygen and water vapors does not ignite, but it yields a reaction product containing 30.1 percent fluorine in 1 1/2 hours. Of this fluorine 10.8 percent is converted by means of hydriodic acid; 20 per cent ~~in~~ round-numbers remain combined.
- 210 Norite combines with fluorine as above in quiet reaction; the final product contains 37.7 percent fluorine after 1 1/2 hours, 5.2 percent of which can be eliminated by means of hydriodic acid.
- 280 As above; the final product has 46.7 percent fluorine. No further reaction with hydriodic acid.
- 320 As above; lively explosion after five minutes.
- 280 The norit acts as above; fluorine pressure of 25 millimeters in the reaction tube. (Fluorine free from O₂.)
 (a) 55.6 percent fluorine after 3 hours (estimated through the decomposition of the reaction product with sodium in a small iron tube; see below).
 (b) 57.3 percent fluorine after ⁴/₈ hours as above; ~~corres-~~ ^{the}ponding to C : F = 1.18 : 1. Hydriodic acid has no effect with respect to a and b.

DEGREES C

400°C Lively sudden decomposition from time to time.

These experiments show how important oxygen and water vapor content are for the reactivity of norite. CF is best obtained from completely degassed norite under reduced pressure (approximately 25 mm) and at a temperature not much higher than 280°C, using oxygen-free fluorine. Graphite is very much less sensitive. In spite of this, its oxygen content has great significance with respect to its reactivity; this becomes evident from the fact the appearance of CO₂ and possibly also COF₂ at the beginning of the reaction with fluorine⁷.

B. The Gaseous Products of Fluoridization

Any oxygen contained in graphite and norite as surface oxygen or water vapor, or which has been introduced with fluorine, appears in the reaction products as CO₂ or COF₂. The COF₂, a gas readily hydrolyzed by water, attacks quartz glass especially at higher temperatures, and therefore always causes formation of SiF₄ when passing through glass apparatus. (O. Ruff and G. Miltshitzky, in a still unpublished contribution.)

Procedure: The fluorine is first of all removed from the gases collected during the fluorination of graphite and norite by pumping it off, keeping the temperature down to that of liquid air. Next they are conducted into a larger flask equipped with a stopcock, where they are agitated with 2 N NaOH for the purpose of eliminating CO₂, COF₂ and SiF₄, and finally condensed again and fractionated from a copper block at different temperatures and pressures.

Table 2 illustrates the composition of the gaseous reaction products in percentages by volume.

Table 2
COMPOSITION OF GASEOUS REACTION PRODUCTS IN PERCENTAGES BY VOLUME

CARBON TYPE	CF ₄	C ₂ F ₆ /C ₃ F ₈	C ₂ F ₄	HIGHER MOLECULAR FLUORIDE
Air Containing Graphite 700° degrees	88.9	7.1	2.5	Not estimated 1.5
Air Containing Norit 400° degrees	84.2	8.3	2.1	Not estimated 5.4
Air Containing Norit 700° degrees	90.0	7.1	1.5	Not estimated 0.9

(2) We have obtained the higher molecular fluorides in the form of an oily liquid

(2) We have obtained the higher molecular fluorides in the form of an oily liquid at room temperature; for clarity's sake we converted them all to the gaseous condition and calculated them as if the oil had uniformly consisted of the compound C₄F₁₀ [see below].

(3) Smooth course of reaction.

(4) Lively sudden decomposition from time to time, accompanied by considerable losses of norite.

The percentage of higher carbon fluorides decreases with rising reaction temperature. The slight difference in the composition of noritic and graphitic gases (at 700 degrees) may have been caused by the greater reaction rate of norit and, as a consequence of this, also by the higher combustion temperature inside the norit. (In spite of the same temperature prevailing in the reaction chamber), and to a lesser extent because of differences in the order magnitude of their carbon atoms.

C. Analyzing ~~the~~ Carbon Monofluoride

Tests made with a view of basing an analysis on the thermal decomposition of CF (see below), in which connection the entire fluoride content is liberated in the form of gaseous fluorides, have failed because of the difficulty in estimating the exact fluoride content in the residual gas.

A measured amount of CF placed in a nickel boatshaped tray was slowly heated in a quartz tube under high vacuum to ~~1000 degrees~~ and allowed to remain there for one hour. The gases developed were condensed in liquid air. The remaining graphite was mixed with Na_2O_2 , the mixture slowly melted and the molten substance obtained dissolved in H_2O ; it was no longer possible to precipitate F⁻ in the solution by means of lanthanum acetate. The gases were decomposed by heating in an evacuated quartz tube containing an iron boatshaped tray completely filled with degassed sodium. NaF plus carbon were produced. Excess sodium was decomposed by alcohol, the NaF dissolved by adding water and the solution then filtered from the carbon. The fluoride in the solution was precipitated and analyzed as PbClF . The values found varied widely; they were some 10 percent lower than the lowest value determined through weight increases in the fluorization process. We found the error in the incomplete decomposition of the gases with sodium; in this connection a minute residual pressure of about 10 millimeters of mercury always remained which could not be taken into consideration in the test portion, since we were not acquainted with the fluoride content of this residual gas.

After additional futile tests aiming at the combustion of fluoride in a mixture of Na_2O_2 and NaOH, the following method was adopted:

Fluoride was placed on the bottom of a 12 centimeter long iron tube of 10 millimeters diameter, welded at one end; in front of which we placed a bulb of metallic sodium at a distance of some 2 centimeters.

Now we welded the other open end while the substance and the sodium had been prevented from too early decomposition by intense cooling with ice.

The entire length of the sealed tube was kept at 800-900 degrees for ten minutes. Upon cooling off the tube center was filed apart and broken open; the tube parts were placed in alcohol to dissolve excess sodium, after which they were leached out with water. The carbon and some iron were then filtered off the solution; F was precipitated from the solution in the form of $PbClF$.

Applied: 0.0585 gram of the substance; found 0.4807 gram of $PbClF$ corresponding to 59.3 percent of F; calculated CF: 61.3 percent.

We had to give up determining the carbon content since we had no reliable methods at our disposal. The ratio found for fluoride yields the atom relation $C : F = 1.085 : 1$.

D. Thermal Decomposition of Graphitic and Neritic Fluoride

The process of decomposing CF depends mainly on the experimental conditions, especially when working with graphitic fluoride. It yields other products under reduced pressure and at lower temperatures than during detonation processes; again, other products are obtained when neritic fluoride is used.

1. Explosive decomposition of graphitic fluoride.

The products of this process can be obtained in the apparatus illustrated in Figure 4 (Decomposition of CF).

A quartz receptacle Q of about 30 millimeters diameter and 100 millimeters length contains a copper tray -- as well attached as possible -- about 3 centimeters high. The top of Q is connected on one side with a horizontal glass tube R (containing CF) by means of a rubber tubing and, on the other side with the gas delivery tube A and condensing tube F cooled by means of liquid air and connected with a vacuum pump through stopcock II.

The apparatus is evacuated and filled with H_2 until a pressure of 1 atmosphere is reached; now asbestos board D is fitted from below around C, and the bottom of C is heated by gas blast to a bright red glow. Next by lifting R minute portions of CF are sprinkled in and are immediately decomposed accompanied by glowing, detonations and soot formation. The gases flow towards F where they become condensed. In conclusion, gases still remaining in C are driven without loss toward F (where they become condensed) by alternately opening and closing stopcocks II and I.

The gases condensed in F are immersed into a cold bath and brought to a temperature of -110° .

degrees, and the portions still volatile at this temperature are drawn into another receptacle cooled with liquid air, under a pressure of < 1 millimeter. The gas thus transferred is then agitated at room temperature successively with water, 2 N-NaOH and Bromine water. After each agitation the gas is again condensed in a glass receptacle filled with liquid air. This is followed by replacing the liquid air by a cold bath of -110 degrees, and the gas is drawn off again. In this manner we gradually liberate the gas from water and ascertain its volume in a satisfactory manner. The volume differences observed yield the amount of gas which has been absorbed by H_2O , 2 N-NaOH and the solution of bromine, that is to say, by SiF_4 , CO_2 and the unsaturated carbon fluorides. The composition of the residual mixture of saturated fluorides is revealed by its density or molecular weight, respectively.

We have obtained from 0.500 gram of CF: (a) at -110 degrees not volatilized: nothing; (b) at -110 degrees volatilized: 59.4 cubic centimeters of gas, of which 5.7 cubic centimeters were CO_2 , 12.1 cubic centimeters C_2F_6 and 41.6 cubic centimeters CF_4 . The coal-like residue is of the finest soot. Thus it will be seen that the average composition of the gaseous mixture corresponds to about the atomic relation of $CF_{3.67}$, on the assumption that the 5.7 cubic centimeters of CO_2 were originally CF_4 .

2. Decomposition of Graphitic Fluoride in High Vacuum.

This type of decomposition also may be carried out in the apparatus just described, except that a manometer is inserted at L and a double length of ~~is used~~. Also, Q is slowly heated in a small electric oven only when the substance has been sprinkled into the cold copper inserted tray. The apparatus completely evacuated, cock III closed and F cooled in liquefied air. ~~The~~ ~~decomposes~~ very slowly at about 300 degrees, being most intense between 500 and 600 degrees. Eventually, a very small amount of uncondensable gases is produced (CO), until a pressure of about 3 millimeters has been reached; at 1000 degrees, the temperature was maintained for one hour.

The residue consists of pure graphite, as can readily be ascertained by an X-ray picture.

The gas analysis yielded the following from 0.5870 grams of CF:

(a) At -110 degrees, unvolatilized, 0.1072 grams = 18.2 percent of the test portion; the molecular weight of the portion gaseous at room temperature, was 288, corresponding to about 8.3 cubic centimeters of C_5F_{12} or C_6 similar fluorides.

(b) at -110 degrees volatilized: 44.3 cubic centimeters of gas, consisting of 9.1 cubic centimeters of SiF_4 , 5.2 cubic centimeters of CO_2 , 4.4 cubic centimeters of C_2F_4 , 17.4 cubic centimeters of C_2F_6 , and 8.2 cubic centimeters of CF_4 . Thus it will be seen that the average composition of the gases corresponds to about the atomic relation of $CF_{2.81}$, if instead of SiF_4 the same amount of CF_4 is employed in the calculations, while the small amount of CO (corresponding to a pressure of 3 millimeters) and 5.2 cubic centimeters of CO_2 are discarded.

3. Decomposition of Noritic Fluoride.

The behavior of this fluoride differs with heating, as test-tube heating does not decompose the fluoride explosively, but produces small fulminations without soot production. We have decomposed fluoride in high vacuum only and obtained from 0.400 grams of CF₄:

- (a) at -110 degrees, unvolatilized fluoride: 0.0734 grams corresponding to about 5.7 cubic centimeters of C₅F₁₂.
- (b) at -110 degrees, 38.6 cubic centimeters of volatile gases, consisting of 16.7 cubic centimeters of SiF₄, 13.2 cubic centimeters of CO₂, 3.6 cubic centimeters of C₂F₄ and 5.1 cubic centimeters of CF₄, C₂F₆ and C₃F₈, with a molecular weight of 149.

The average composition of these gases corresponds to about the atomic relation of CF < 2.7g, provided that for 16.7 cubic centimeters of SiF₄ the same amount of CF₄ is used and the CO₂ amount obtained remains discarded. The fluorine number of the atomic relation is perhaps still somewhat too high, since a brown colored distillate was precipitated in the delivery tubes of the incandescent chamber, soluble in acetone and benzene, giving off the odor of hydrogen fluoride when heated. Black, light-weight flakes were produced near the hot zone. These were resistant to alkali and mineral acids and when heated in air burst into an intensely bright flame.

Again the residue resembled norit, but the X-ray analysis and the determination of its specific conductivity revealed its strongly graphitic nature (See Section F.).

Thus it will be seen that the thermal decomposition of graphitic CF yields a gaseous mixture rich in CF₄ at higher temperatures and runs a correspondingly explosive course; this gaseous mixture has an average atomic relation of CF₄ at the lowest possible temperature or in high

vacuum, but it compensates for this by yielding considerable amounts of higher fluorides the highest of which even exceeds C_9F_{12} , in agreement with the average atom relation $CF_{2.81}$. The residue consists of pure graphite. If noritic CF is decomposed in high vacuum at the same temperature, still larger amounts of higher fluorides are produced (corresponding to the atomic relation $CF < 2.78$) in addition to some brown distillate.

B. Properties of Carbon Monofluoride, CF

CF is gray colored, regardless of ~~the fact~~ whether it is obtained from graphite or from norit.

The specific gravity of graphitic CF with a fluorine content of 59.3 percent, is 2.39; that of pure CF has been accordingly estimated from the law of mixtures as ~ 2.40 (calculated by the X-ray photographic method, as stated in the Introduction, ~~we have~~ 2.43).

The determination was carried out in a pycnometer attached to a high vacuum apparatus. A glass tube fused on to the ~~neck~~ terminated in a sealed capillary dipped into purest xylene. After the air had been drained entirely from the apparatus by pumping, the capillary was broken off by tweezers ~~underneath~~ the surface of the xylene. And so pure xylene found its way into the pycnometer without being first exposed to the air; in this manner the adherence of air bubbles to CF has been eliminated.

CF is insoluble in the usually employed solvents, unwettable with water and aqueous solutions, wettable with fluids such as benzene, acetone, alcohol, glacial acetic acid, etc. No change in the weight occurs in high vacuum at room temperature. Aqueous acids and bases do not attack the fluoride. Only heating, decomposition with oxidizing melts (as for instance $H_2O_2 + NaOH$) or metallic sodium will destroy it entirely.

It is insensitive to H_2 at 400 degrees and to aqueous hydriodic acid.

Zinc dust and glacial acetic ^{acid} reconvert fluoride into the original carbon form; this process is quicker with substances obtained from norit, as may be expected from the different ^{surface} development of the two forms:

A mixture of 0.5 gram of Cf obtained from graphite, 2 grams of zinc dust, and 20 grams of glacial acetic ^{acid} to which further portions of zinc dust were added whenever necessary -- must be boiled for about 20 hours ^{until} the graphite formed ~~during the fusion~~ with sodium is found to be free from fluorine. An equal amount of Cf obtained from norit is freed from fluorine in as little as six hours under the same conditions.

Fl can be precipitated from glacial acetic ^{acid} by calcium acetate.

The dry residue obtained from reducing 0.5 gram of graphitic fluoride yields in the annealing process 8.5 cubic centimeters of gas (H_2) uncondensable in liquid air; the residue from 0.5 gram of noritic fluoride yields about 2.7 cubic centimeters, but also about 13 cubic centimeters of another gas readily condensable by cooling, having a molecular weight of about 76, that is, probably benzene. The residue obtained from graphitic Cf, when ~~pressed together~~ ^{pressed together} by 120 atmospheres (see below), has a specific resistance of about 1.25 Ω . (graphite has 0.03 Ω ; Cf $> 3000 \Omega$ as stated in Section F). Thus it will be seen that the metallic bond is again present. X-ray analysis also reveals the residue ^{is} graphite. In contrast, the residue obtained from reducing noritic Cf is found almost lacking in interference, as is the case with the norit in the initial stages.

Electrical conductivity: the powder to be analyzed is subjected to a pressure of 120 atmospheres in a porcelain tube with thick walls, protected by a steel tube; the ^{plates} ~~press-plate~~ and base made of steel serve as power supply. The measuring process is carried out ^{with} ~~through~~ the usual bridge connection. We have also determined, for the sake of com-

parison, the resistance offered under the same conditions by our graphite, pure norit, and norit obtained from annealing noritic CF in high vacuum,

- (a) Specific resistance of pure norit₂ at 1/0 atmospheric pressure: 82 Ω .
- (b) The same for CF obtained from norit or graphite: > 300 Ω .
- (c) The same for the residue obtained from annealing noritic CF: 0.43 Ω .
- (d) The same for the residue obtained from annealing graphitic CF: 9.03 Ω .

The high specific resistance reveals the fluoride to be a physical compound.

Adsorptive power for noritic CF: Only absolute alcohol solutions have been used, since CF is not wettable by water.

- (a) Adsorptive power with respect to HCl: 0.1 gram of the substance has been agitated with 10 cubic centimeters of 2%/10-HCl for 24 hours at 25°C, and then centrifuged. The HCl content was determined by titration.

	FINAL CONCENTRATION (NORMALITY)	ADSORBED AMOUNT (IN MILLIGRAMS)
Pure norit	0.1345	0
Carbon-1-fluoride obtained from norit	0.1345	0

- (b) Adsorptive power with respect to NaOH: carried out in accordance with (a).

	FINAL CONCENTRATION (NORMALITY)	ADSORBED AMOUNT (IN MILLIGRAMS)
Pure norit	0.1078	0.195
Carbon-1-fluoride obtained from norit	0.0411	0.862

- (c) Adsorptive power with respect to methylene blue: carried out in accordance with (a). The methylene blue content was determined by colorimetric methods.

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	FINAL CONCENTRATION IN MILLIGRAMS PER CUBIC CENTIMETER	ADSORBED AMOUNT IN MILLIGRAMS
Pure norit	0.01	1.99
Carbon-1-fluoride obtained from norit	0.20	0.00
Annealed carbon-1-fluoride obtained from norit	0.10	1.00
Carbon-1-fluoride obtained from norit, reduced with Zn	0.0002	1.998

(d) Adsorptive power with respect to phenol: carried out in accordance with (a). The phenol content has ~~been~~ determined by titration (see Beckurts's Volumetric Analysis, 8th edition, page 420).

	FINAL CONCENTRATION IN MILLIGRAMS PER CUBIC CENTIMETER	ADSORBED AMOUNT IN MILLIGRAMS
Pure norit	49.65	1.0
Carbon-1-fluoride obtained from norit	49.65	1.0

The purpose in carrying out adsorption tests was to arrive at a rough idea of the range change in the adsorptive power of norit made possible by the incorporation of fluorine ions; it should be understood that such tests must still be carried out on a larger scale.

Remarks. The adsorptive power of carbon-fomas with respect to phenol (from aqueous solutions), obtained through the decomposition of noritic CF₂ 0.1 gram of the substance, ~~has been~~ agitated for 24 hours at 25 degrees with 10 cubic centimeters solution, and then centrifuged. The phenol content ~~has been~~ determined by interferometric methods. Initial solution = 50 milligrams of phenol per cubic centimeter.

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	FINAL CONCENTRATION IN MILLIGRAMS PER CUBIC CENTIMETER	ADSORBED AMOUNT IN MILLIGRAMS
Pure norit	46.75	32.5
Reduced CF obtained from norit	48.13	18.7
Reduced CF obtained from graphite	48.90	11.0
Soot obtained from graphite	49.06	9.4

F. Roentgenograms.

The roentgenogram of graphitic CF shows the interferences of prismatic surfaces 1070, 1120 only; the roentgenogram of noritic CF shows the same interferences but with corresponding granular diminution. The interferences of the basal surfaces are missing in both cases.

Semifluorized graphitic CF with 32 percent F yields the same formation. Interferences in the basal surfaces have almost disappeared in the fog density. Thus it will be seen that there is no intermediate stage in fluorination, nor does a gradual widening in the interval of the basal surfaces occur.

Soot obtained from the rapid decomposition of graphitic CF just reveals the outlines of the basal interferences; on the other hand, the high vacuum residue of the same CF yields all the graphitic interferences; thus the latter consists of graphite.

Summary

At not too high temperatures fluorine produces a tight valence compound having the limiting combination CF with carbon of any grade of order. This compound is obtained by saturating, for instance oxygen-free norit at 280[°] ~~degrees~~ with fluorine of 25 millimeters pressure, and fine graphite at 420[°] ~~degrees~~ under 760 millimeters pressure. Two fluorine ions have been incorporated into the compound, between the basal surfaces of the graphite, for every two C-atoms. The structure, the physical and

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chemical properties of the fluorides have been described. Gaseous C-
fluorides have been obtained from corundum and graphite and, naturally,
also from CF₄ at higher temperatures. Their method of preparation has
been elucidated and their composition with respect to the conditions of
production has been determined.

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Received by the Editor on 10 December 1933.

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