

# Poly(carbon monofluoride): A Solid, Layered Fluorocarbon

PETER KAMARCHIK, JR., and JOHN L. MARGRAVE\*

Chemistry Department, Rice University, Houston, Texas 77001

Received July 12, 1976<sup>†</sup>

Poly(carbon monofluoride),  $\text{CF}_x$ ,<sup>1</sup> is a nonstoichiometric solid fluorocarbon whose formula can vary from  $\text{CF}_{x \approx 0}$  to  $\text{CF}_{x=1.24}$ . There has recently been a great deal of interest in  $\text{CF}_x$  of both a theoretical and a practical nature. It has been shown to be a superior lubricant<sup>2-4</sup> under the extreme conditions of high temperature and high vacuum. It has also been used quite successfully as a cathodic depolarizer in high-energy density batteries<sup>5-9</sup> and has been used as a gas chromatographic stationary phase.<sup>10</sup>

The color varies with fluorine content and is black for fluorine/carbon ratios up to about 0.9, gray from 0.9 to 1.0, and white above 1.0.  $\text{CF}_x$  was first discovered by Ruff, Bretschneider, and Ebert in 1934.<sup>11</sup> By heating graphite in a stream of  $\text{F}_2$  to 420–460 °C a gray product was formed with a composition  $\text{CF}_{0.92}$ . Later Palin and Wadsworth<sup>12</sup> prepared under conditions similar to those of Ruff a compound analyzed as  $\text{CF}_{1.04}$ . The Rudorffs then took up the work and were able to prepare compounds which ranged in stoichiometry from  $\text{CF}_{0.68}$  to  $\text{CF}_{0.99}$ .<sup>13</sup> By 1974, Margrave et al.<sup>14</sup> had reported an upper limit of 1.12 for the F/C ratio in  $\text{CF}_x$  prepared in a high-temperature reaction between gaseous fluorine at 1 atm and graphite. Presumably the excess fluorine is being bound at edge carbon sites for which two bonding positions are available. The conditions for preparing this composition of  $\text{CF}_x$  are a temperature of 627 °C and at least 1.5 times as many moles of  $\text{F}_2$  as moles of C. Slightly higher fluorine contents have been obtained by the use of a chlorine/fluorine mixture.<sup>15</sup>

## Structure

The determination of the structure of  $\text{CF}_x$  has presented a great deal of difficulty from the earliest work of Palin and Wadsworth<sup>12</sup> to the present. The great difficulty encountered in growing single crystals has contributed to this problem. Watanabe<sup>5</sup> et al. have succeeded in growing a few small crystals which proved inadequate for a detailed single-crystal X-ray structural analysis; however, their work and a recent X-ray powder diffraction study done by Mahajan, Badachhappe, and Margrave<sup>16</sup> indicate a hexagonal crystal lattice with  $a_0 = b_0 = 2.530 \pm 0.005$  Å;  $c_0 = 5.760 \pm 0.002$  Å; and  $\gamma = 118.8 \pm 0.5^\circ$ . It was found that the normally diffuse  $\text{CF}_x$  lines could be made much sharper by pressing and heating the samples in a tetrahedral high-pressure

Table I  
Comparison of Observed and Calculated  $d$  Spacings  
for a Hexagonal Lattice<sup>a,16</sup>

	Intensity	$2\theta$	$d$ spacing		Planes $hkl$
			Obsd	Calcd	
1	S	15.375	5.763	5.760	001
2	MS	31.05	2.880	2.880	002
3	MS	40.65	2.219	2.219	100
4	MW	47.175	1.926	1.921	003
5	MW	64.95	1.435	1.440	004
6	MS	73.40	1.289	1.281	110
7	VW	87.75	1.112	1.109	200
8	VVW	132.40	0.843	0.839	210

<sup>a</sup> Hexagonal lattice parameters:  $a = b = 2.530 \pm 0.005$  Å;  $c = 5.760 \pm 0.002$  Å;  $\gamma = 118.8 \pm 0.5^\circ$ .

device<sup>17</sup> at 20 kbar and 150 °C for 20 h. Figures 1 and 2 show several views of the structure proposed by Mahajan et al. The unit cell has a volume of  $32.31$  Å<sup>3</sup>. The C–C distance has increased from 1.41 Å in graphite to 1.47 Å in  $\text{CF}_x$ . The C–C–C bond angle has been calculated to be  $118.8^\circ$  compared to  $120^\circ$  in graphite.

<sup>†</sup> Revised received November 7, 1977.

(1) (a) Abstracted in part from the Ph.D. Thesis of Peter Kamarchik, Jr., Rice University, Houston, Texas, May 1976. (b) Also known as graphite fluoride, fluorographite, and "CFX". (c) CFX, Registered U.S. Trademark.

(2) R. L. Fusaro and H. E. Sliney, "Graphite Fluoride: A New Solid Lubricant", NASA Technical Memorandum, NASA TM X-52624, 1969.

(3) R. L. Fusaro and H. E. Sliney, "Graphite Fluoride As a Solid Lubricant in a Polyimide Binder", Lewis Research Center Technical Report, 1971.

(4) H. Gisser, M. Petronio, and A. Shapiro, *J. Am. Soc. Lubr. Eng.*, **28**, 161 (1972).

(5) (a) N. Watanabe and M. Takashima, Proceedings of the 7th International Symposium on Fluorine Chemistry, Santa Cruz, Calif., July, 1973; (b) N. Watanabe, Y. Koyama, and S. Yoshizawa, *J. Electrochem. Soc. Jpn.*, **32**, 17 (1964).

(6) (a) K. Brauer, Electrochemical Society Extended Abstracts, Spring Meeting, Boston, Mass., May 1969, Abstract No. 210, p 495; (b) Abstract No. 64, p 401; (c) K. Brauer, "Feasibility Study of the Lithium/C<sub>2</sub>F Primary Cell", R&D Technical Report ECOM-3322, August 1970; (d) K. Brauer and K. R. Moyes, U.S. Patent No. 3514337, May 1970.

(7) (a) N. Watanabe and M. Fukuda, *Chem. Abstr.*, **72**, 38270n (1970); (b) M. Fukuda, and T. Iijima, Electrochemical Society Extended Abstracts, Fall Meeting, Cleveland, Ohio, Oct 3–7, 1971, Abstract No. 41, p 100.

(8) I. Takashi and T. Yoshinori, Japanese Patent No. 7550631, May 7, 1975.

(9) H. F. Hunger and G. J. Heymach, *J. Electrochem. Soc.*, **120**, 1161 (1973).

(10) L. C. Swope and E. A. Smith, U.S. Patent No. 3877894, April 15, 1975.

(11) O. Ruff, O. Bretschneider, and F. Ebert, *Z. Anorg. Allgm. Chem.*, **217**, 1, (1934).

(12) D. E. Palin and K. D. Wadsworth, *Nature (London)*, **162**, 925 (1948).

(13) (a) W. Rudorff and G. Rudorff, *Z. Anorg. Allgm. Chem.*, **253**, 281 (1947); (b) W. Rudorff and G. Rudorff, *Chem. Ber.*, **80**, 413 (1947); (c) W. Rudorff in "Handbook of Preparative Inorganic Chemistry", Vol. 1, G. Brauer, Ed., Academic Press, New York, N.Y., 1963, p 635; (d) W. Rudorff, *Adv. Inorg. Chem. Radiochem.*, **1**, 223 (1959).

(14) R. J. Lagow, R. B. Badachhappe, J. L. Wood, and J. L. Margrave, *J. Chem. Soc., Dalton Trans.*, 1268 (1974).

(15) P. Kamarchik, Jr., Ph.D. Thesis, Rice University, Houston, Texas, May 1976.

(16) V. J. Mahajan, R. B. Badachhappe, and J. L. Margrave, *Inorg. Nucl. Chem. Lett.*, **10**, 1103 (1974).

(17) (a) R. B. Badachhappe, P. J. Ficalora, R. G. Bautista, and J. L. Margrave, "Chemical Methods of Preparing Diamonds", U.S. Patent No. 3711595, Jan 16, 1973; (b) C. H. Chang and J. L. Margrave, *J. Am. Chem. Soc.*, **90**, 2020 (1968); (c) C. H. Chang, Ph.D. Thesis, Rice University, Houston, Texas, 1967.

John L. Margrave is Professor of Chemistry and Dean of Advanced Studies and Research at Rice University. He was born in Kansas City, Kansas, in 1924, and studied at the University of Kansas for both his B.S. and Ph.D. degrees. Dr. Margrave has been interested in the chemistry of fluorine compounds for several years; his interests have ranged from thermodynamic properties to optical spectroscopic and high temperature properties.

Peter Kamarchik, Jr., is a Research Chemist at PPG Industries in Pittsburgh, Pa. He studied at Carnegie-Mellon University for his undergraduate degree and completed the Ph.D. at Rice University in 1976 with Dr. Margrave. He has specialized in studies of fluorine compounds and particularly of the layered fluorocarbon discussed in this Account.

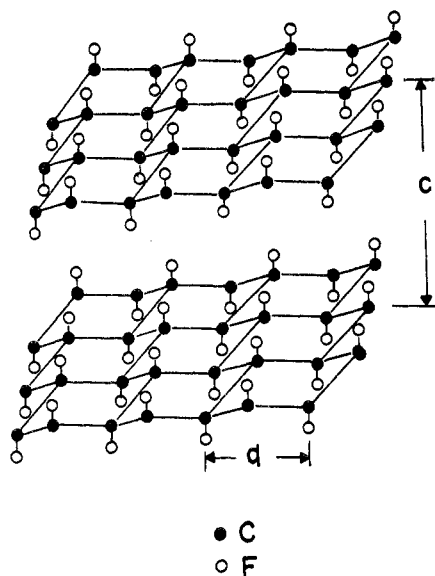


Figure 1. Structure of "chair"  $\text{CF}_x$ .<sup>16</sup> "a" and "c" refer to the unit cell axes.

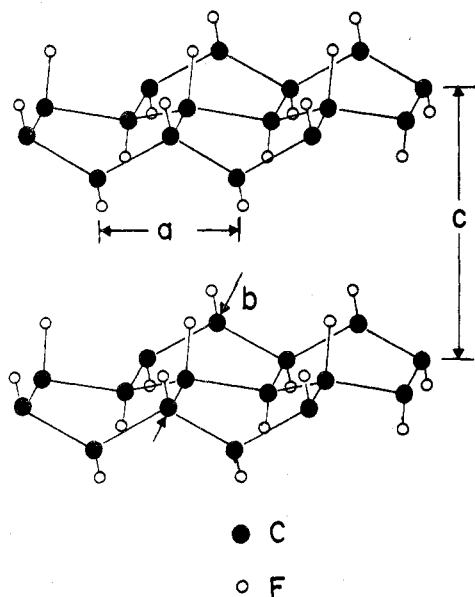


Figure 2. Structure of "boat"  $\text{CF}_x$ .<sup>18</sup> "a", "b", and "c" refer to the unit cell axes.

The total absence of (*hkl*) reflections indicates a turbostratic structure, i.e., no regular stacking of the CF layers with respect to one another.

Ebert<sup>18</sup> has criticized this structure on the basis of solid-state  $^{19}\text{F}$  NMR data for various  $\text{CF}_x$  samples. Recognizing the most common configurations of six-membered, saturated carbon rings, Ebert calculated hypothetical NMR second moments for  $\text{CF}_x$  consisting of an infinite array of cyclohexane "chairs", as Mahajan et al. proposed, and for an infinite array of "boats". In both cases, fluorine atoms were assumed to be covalently bonded to carbon above and below the carbon planes (see Figures 1 and 2). The "boat" structure gives a calculated second moment of  $21.7 \text{ G}^2$  and the "chair" structure gives a second moment of  $10.3 \text{ G}^2$ . A comparison with the experimental value of  $24.2 \pm 1.2 \text{ G}^2$  favors the "boat" structure.

(18) L. B. Ebert, Ph.D. Thesis, Stanford University, Stanford, Calif., 1975, Chapter VIII.

Table II  
Heats of Formation and Entropies for  
Various  $\text{CF}_x$  Compounds<sup>20,21</sup>

	$\Delta H_f^{\circ},_{298}$ kJ/mol	$S_{298}$ J/(molK)
$\text{CF}_{1.125}$	-195.73	13.64
$\text{CF}_{0.597}$	-101.74	14.71
" $\text{C}_4\text{F}$ "; $\text{CF}_{0.297}$	-25.43	11.22

The symmetry of the "boat" structure would result in an orthorhombic crystal lattice with  $a_0$  and  $b_0$  axes as shown in Figure 2. A calculation of the  $d$  spacings predicted for the first 40 low-order reflections of an orthorhombic cell with  $a_0 = 2.47 \text{ \AA}$ ,  $b_0 = 4.11 \text{ \AA}$ , and  $c_0 = 5.76 \text{ \AA}$  predicts only the (00*l*) diffraction lines. These distances were calculated on the basis of ordinary C-C and C-F covalent bond lengths and  $\text{sp}^3$ -hybridized carbon. These predicted lines, however, are independent of the choice between a hexagonal lattice or an orthorhombic lattice. The good agreement between calculated and observed diffraction lines, assuming a hexagonal lattice, is shown in Table I. Unfortunately a hexagonal lattice is not compatible with the symmetry of the "boat" structure implied by the NMR data. The apparent contradiction between this result and the NMR results can be resolved, in one way, by a reconsideration of the calculated second moment values. One notes that the only feature of the boat structure that is necessary to yield a calculated second moment value of approximately  $20 \text{ G}^2$  is the close approach of the fluorine atoms ( $1.64 \text{ \AA}$ ) bonded at the (1-4) carbon position. If this kind of close approach of fluorine atoms could be obtained in a chair structure, the NMR data could be explained and the hexagonal crystal lattice could still be maintained. A possible means of achieving this was suggested by Mahajan, Badachhape, and Margrave,<sup>16</sup> i.e., there could be  $\text{F}_2^{\delta-}$  or  $\text{F}_3^{\delta-}$  species present between the carbon layers. It appears that on the basis of the present data a structure for  $\text{CF}_x$  cannot be conclusively determined.

### Thermodynamic Data

Margrave and co-workers have employed fluorine bomb calorimetry to determine the heats of formation of various  $\text{CF}_x$  type compounds.<sup>19-21</sup> Low-temperature heat capacity measurements have also been made.<sup>20-21</sup> The heats of formation and absolute entropies at 298 K are given in Table II. The molar heat capacity of  $\text{CF}_{0.597}$  shows a slight dependence on the thermal history of the compound which could be due to the existence of two phases,<sup>21</sup> one stable at low temperature and the other stable at room temperature. A transition between these two phases would presumably be very slow. The heat capacities of all three compounds show the same anomalous behavior as graphite in that the Debye function is not followed in the vicinity of 0 K. A function of the form:

$$C_p = aT^2 + bT^3 + cT^4 + dT^5 + \dots$$

(19) J. L. Wood, R. B. Badachhape, R. J. Lagow, and J. L. Margrave, *J. Phys. Chem.*, **73**, 3139 (1969).

(20) J. L. Wood, A. J. Valerga, R. B. Badachhape, and J. L. Margrave, "Thermodynamic, Electrochemical, and Synthetic Studies of the Graphite-Fluorine Compounds  $\text{CF}$  and  $\text{C}_4\text{F}$ ", U.S. Army Electronics Command, Research and Development Technical Report, ECOM-0105-F, Dec 1972.

(21) A. J. Valerga, R. B. Badachhape, G. D. Parks, P. Kamarchik, J. L. Wood, and J. L. Margrave, "Thermodynamic and Kinetic Data of Carbon-Fluorine Compounds", U.S. Army Electronics Command, R&D Technical Report, ECOM-0056-F, March 1974.

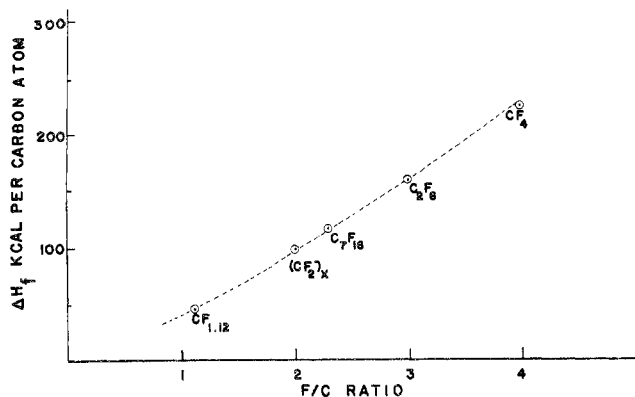


Figure 3. Variation in heat of formation with F/C atomic ratio.

can be used to fit the data. The usual Debye function is of the form

$$C_p = AT^3 + BT^5 + CT^7 \dots$$

Attempts have been made to correlate the heats of formation of saturated fluorocarbons with their F/C ratios.<sup>19</sup> Figure 3 shows a plot of  $\Delta H_f$  vs. F/C ratio for  $CF_{1.12}$ ;  $(CF_2)_x$  (Teflon);  $C_7F_{16}$ ,<sup>22</sup>  $C_2F_6$ ,<sup>23</sup> and  $CF_4$ .<sup>24</sup> Wood et al.<sup>19</sup> suggest the use of the formula

$$\Delta H_f(CF_x) = -(44x + 3x^2) \pm 3 \text{ kcal mol}^{-1}$$

but the simple linear relationship

$$\Delta H_f^\circ(CF_x) = -61.66x + 22.30 \text{ kcal mol}^{-1}$$

gives a better fit to the observed data. The  $\Delta H_f^\circ$  values for  $CF_{0.60}$  and  $CF_{0.24}$  do not fit either of these formulations well and may indicate a certain amount of residual unsaturation of the carbon atoms in these compounds. If a formula is to be used to calculate  $\Delta H_f^\circ$  for  $CF_x$  where  $x$  runs from about 0.6 to 1.12 it would probably be best to use the  $\Delta H_f^\circ$  for these compounds to define a linear relationship which can be expressed as

$$\Delta H_f^\circ(CF_{x,s}) = -42.55x + 1.08 \text{ kcal mol}^{-1}$$

In the same way the total entropy can be given as

$$S_{298}(CF_{x,s}) = 4.04x + 1.10 \text{ cal K}^{-1} \text{ mol}^{-1}$$

### Electron Spectroscopy Studies of $CF_x$

The valence band structure of  $CF_x$  has been probed by Thomas et al.,<sup>25</sup> who reported a good agreement between theoretically computed and the experimentally measured density of states. The polarization of the C-F bond was found to be  $q_C = -q_F = 0.4(e)$ . The ESCA spectra reported by Clark<sup>26</sup> and those observed by Parks<sup>27</sup> are in close agreement and indicate covalent

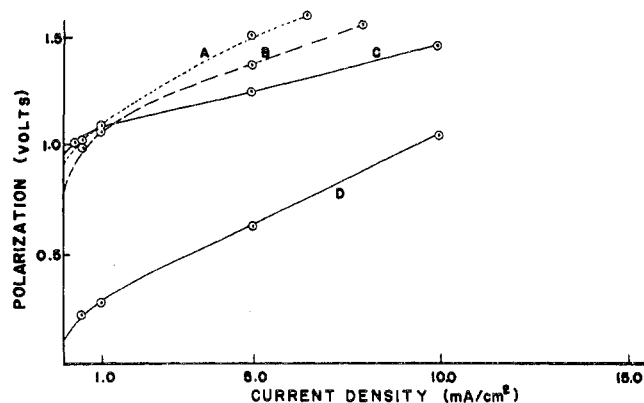


Figure 4. Polarization curves for various cathodes in Li/1 M  $LiClO_4$ -polycarbonate cells.<sup>9</sup> (A)  $C_{5.54}F$ ;  $T = 29.8^\circ C$ ; (B)  $C_8O_{1.48}(OH)_{1.48} \cdot 1.44 H_2O$ ;  $T = 29.5^\circ C$ ; (C)  $CF$ ;  $T = 29.0^\circ C$ ; (D)  $MnO_2$ ;  $T = 26.0^\circ C$ . Reprinted with permission from ref 9. Copyright 1973, The Electrochemical Society, Inc.

Table III  
Comparison of Open-Circuit Voltages of Various  
Li/Organic Electrolyte/Depolarizer Cells with emf's<sup>a</sup>

Cell <sup>a</sup>	Open-circuit voltage emf, V	$T, ^\circ C$
Li/1 M $LiClO_4$ -PC/ $C_{5.54}F$	3.32	29.5
Li/1 M $LiClO_4$ -PC/CF	3.14	29.0
Li/1 M $LiClO_4$ -PC/ $C_{x,O_y}H_z$	3.34	28.0
Li/1 M $LiClO_4$ -PC/ $MnO_2$	3.51	24.2
Li/1 M $LiClO_4$ -PC/C graphite	3.00	00
Li/1 M $LiAsF_6$ -PC/CF	2.85	4.66
Li/1 M $LiClO_4$ - $Me_2SO_3$	3.22	4.66

<sup>a</sup> PC, polycarbonate solvent;  $Me_2SO_3$ , dimethyl sulfite solvent.

C-F bonds. Parks has found no dependence of line positions with  $CF_x$  stoichiometry.

### Electrochemical Behavior

The first reported use of a graphite fluoride as a battery material was that of Brauer,<sup>6</sup> who used tetracarbon monofluoride as a cathodic depolarizer in lithium anode-organoelectrolyte batteries. Subsequent investigations by Fukuda and Watanabe<sup>7</sup> and others<sup>9</sup> have demonstrated the potential usefulness of carbon monofluoride-lithium batteries. One of the major difficulties to overcome in the development of a practical battery is presented by the fact that  $CF_x$  is only obtained as a microcrystalline powder, and while gray  $CF_x$  is a poor conductor, white  $CF_x$  is an electrical insulator.<sup>28</sup> These properties necessitate the fabrication of electrodes from mixtures containing the  $CF_x$ , a binder, and a conducting medium (usually graphite). Hunger and Heymach<sup>9</sup> at the U.S. Army Electronics and Devices Laboratory (ECOM) have done extensive testing and have developed a mechanically stable electrode based on  $CF_x$ , graphite, Teflon powder, and DuPont Teflon emulsion 41 BX. They have also done experiments to compare the open-circuit voltages (OCV) and energy densities of carbon monofluoride (CF), tetracarbon monofluoride (actual composition  $C_{5.54}F$ ), graphite oxide [ $C_8O_{1.48}(OH)_{1.48} \cdot 1.44 H_2O$ ], and manganese dioxide, an ordinary cathodic depolarizer. The polarization curves for these depolarizers, shown in

(22) W. D. Good et al., *J. Phys. Chem.*, **63**, 1133 (1959).

(23) G. C. Sinke, *J. Phys. Chem.*, **70**, 1326 (1966).

(24) (a) E. Greenberg and W. N. Hubbard, *J. Phys. Chem.*, **72**, 222 (1968); (b) J. L. Wood, R. J. Lagow, and J. L. Margrave, *J. Chem. Eng. Data*, **12**, 2 (1967).

(25) (a) D. E. Perry, J. M. Thomas, B. Bach, and E. L. Evans, *Chem. Phys. Lett.*, **29**, 128 (1974); (b) P. Cadman, J. D. Scott, and J. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 654 (1975).

(26) (a) D. T. Clark, *Polym. Sci. Technol.*, **5A**, 253 (1974). (b) D. T. Clark, James Peeling, Department of Chemistry, University of Durham, Durham DH1 3LE, England, Applications of ESCA to Polymer Chemistry; *Structure and Bonding in Commercially Produced Fluorographites*, *J. Polym. Sci.*, **14**, 2941-2967 (1976).

(27) G. D. Parks, Ph.D. Thesis, Rice University, Houston, Texas, July 1976.

(28) O. Ruff and O. Bretschneider, *Z. Anorg. Allg. Chem.*, **217**, 1 (1934).

Table IV  
Comparison of Cathodic Depolarizers Discharged in  
Li/1 M LiClO<sub>4</sub>-PC/Depolarizer Cells at 1 mA/cm<sup>2</sup> and  
T = 29.7 °C<sup>a</sup>

Depolarizer	(W-h/ lb) theo- retical <sup>a</sup>	(W-h/ lb) experi- mental <sup>b</sup>	$\bar{V}^c$	$\eta^d$
C <sub>5</sub> F <sub>54</sub>		263	1.85	100
CF	1491	804	2.05	100
C <sub>8</sub> O <sub>1.48</sub> (OH) <sub>1.48</sub>		590	1.87	100
MnO <sub>2</sub>	349	241	2.52	68.3

<sup>a</sup> (W-h/lb) theoretical are based on emf values computed from thermodynamic data and pounds of total cell reactants. <sup>b</sup> (W-h/lb) experimental are based on graphical integration of the discharge curves, up to the utilization efficiency  $\eta$ , and on pounds of depolarizer only. A comparison of this data with <sup>a</sup> gives the loss in theoretical energy content given by the cathodic polarization at the given rate. In the case of CF, e.g., this loss amounts to 46.0%. <sup>c</sup> The average discharge potential  $\bar{V} = (W-h/g)$  experimental/(A-h/g) theoretical. <sup>d</sup>  $\eta$  depolarizer utilization in %.

Figure 4, indicate that the three graphite compounds exhibit the undesirable property of a large polarization even at low current densities. MnO<sub>2</sub> is observed to be a much better depolarizer in this respect. The large polarization in the case of the graphite fluorides may be due to a high activation energy for the reaction



This is not surprising since the breakage of a C-F bond is involved.

Table III shows a comparison of open-circuit voltages and theoretical emf's of various battery systems. Table IV shows a comparison of energy densities for various depolarizers. CF has, by far, the highest energy density of the systems tested and also a high value of average discharge potential. It should be noted, however, that the OCV for CF is considerably less than that predicted on the basis of known thermodynamic data for reaction 1.

Tiedmann<sup>29</sup> has suggested that the lower OCV can be attributed to a mixed potential of the cathodic reaction of CF coupled with the anodic decomposition of the solvents. An alternate explanation has been offered by Whittingham,<sup>30</sup> who argues that, because of the high C-F bond energy, it is unlikely that fluorine can diffuse to the edges of the basal planes fast enough to maintain the observed discharge currents. Therefore, Li must penetrate between the planes, and it is suggested that the initial reaction is the formation of a ternary phase of composition (CLi<sub>n</sub>F), with  $n < 1$ . The observed OCV is then the potential of the reaction



rather than of reaction 1. It is presumed that the CLi<sub>n</sub>F then decomposes to graphite and LiF. In support of this hypothesis, it was observed that samples of white CF<sub>x</sub> turned black almost immediately upon reaction with solutions of lithium naphthalenides in tetrahydrofuran solution, indicating a very rapid reaction. X-ray analysis of the product indicated an expansion from 5.8 to 9.35 Å between the basal planes.

Both Tiedmann<sup>29</sup> and Hunger and Heymach<sup>9</sup> have been concerned with the feasibility of recharging these batteries. They found that, at the potentials required,

the solvents are unstable with respect to oxidation-reduction reactions and are readily decomposed.

### Lubrication Properties

Among the practical applications for CF<sub>x</sub> now under consideration, one of the most promising is its use as a solid lubricating agent. Although lubrication by solids is not well understood, especially the roles played by adsorbed gases and water, certain properties of any proposed lubricant have been found to be of particular importance. Desirable characteristics include thermal stability, low shear strength, surface protection, surface adherence, and lamellar crystal structure. With the exception of good surface adherence, CF<sub>x</sub> possesses these qualities.

In evaluating a material for its lubrication ability, three test properties are generally considered: coefficient of friction, wear life, and rate of wear. Extensive studies have been conducted<sup>2-4,31</sup> in which all three of these properties have been compared for CF<sub>x</sub> of various stoichiometries, graphite, and MoS<sub>2</sub>. The effects of admixing these with different binders have also been evaluated. In the studies using a pin-on-disk friction apparatus, it was found that CF<sub>x</sub> exhibited frictional coefficients less than that of graphite and about equal to that of MoS<sub>2</sub>. In addition, wear life was found to be longer than that of either graphite or MoS<sub>2</sub> over a wide range of conditions of temperature and atmosphere.

Ball-on-disk and Falex tests recently conducted by McConnell<sup>31</sup> have somewhat contradicted these earlier findings. In these types of apparatus, CF<sub>x</sub> has been said to be inferior to MoS<sub>2</sub> by demonstrating considerably higher frictional coefficients while under heavy loads and in varying atmospheres. However, all these tests were carried out at room temperature, and the earlier studies indicated that the greatest advantage in using CF<sub>x</sub> was its properties at elevated temperatures.

It is agreed, though, that under light loads CF<sub>x</sub> is the superior lubricant. It has also been found that stoichiometry, at least in the range CF<sub>0.61</sub> to CF<sub>1.12</sub>, does not affect lubricity.

### Intercalation Compounds

In an attempt to modify the electronic character of graphite, Ebert<sup>32</sup> proposed that the  $\pi$  conduction band could be completely depopulated by the formation of "hole" graphite. This can be represented by (C<sup>+</sup>X<sup>-</sup>)<sub>n</sub>. Experimentally, this involved the reaction of CF<sub>x</sub> with antimony pentafluoride. The idealized complete reaction would yield a planar C<sup>+</sup> ring system with SbF<sub>6</sub><sup>-</sup> anions above and below each carbon ring. Both electrostatic and steric arguments eliminate the possibility of a complete reaction, but do not rule out reaction at a fraction of the available sites.

The experimental results are not conclusive, but a reaction was reported to have taken place. The product was analyzed as CF<sub>1.06</sub>H<sub>0.37</sub>(SbF<sub>5</sub>)<sub>0.09</sub>. The IR showed absorptions not attributable to pure CF<sub>1.06</sub> or to SbF<sub>5</sub> and the powder X-ray diffraction pattern contained lines at 8.2-8.4, 5.2, 4.7, 4.0, and 3.37 Å. The line at 8.2-8.4 Å may correspond to an 001 reflection for the

(29) W. Tiedmann, *J. Electrochem. Soc.*, **121**, 1308 (1974).

(30) M. S. Whittingham, *J. Electrochem. Soc.*, **122**, 526 (1975).

(31) B. D. McConnell, "Characterization of Graphite Fluoride, CF<sub>x</sub>, as a Potential Lubricant Material", Air Force Materials Laboratory Technical Report TR-74-35, Wright-Patterson Air Force Base, Ohio, 1975.

(32) L. B. Ebert, Ph.D. Thesis, Stanford University, Stanford, Calif., 1975, Chapter IX.

SbF<sub>5</sub> intercalated CF<sub>1.06</sub>. This is an area which deserves considerably more investigation and may result in the development of other compounds with useful electrochemical properties.

### Thermal Decomposition

The earliest studies<sup>5b</sup> on the thermal stability of CF<sub>x</sub> consisted merely of finding the minimum temperature at which the decomposition became self-sustaining, i.e., the heat evolved in the decomposition was sufficient to keep the sample at the decomposition temperature. This temperature was found to be about 600 °C. An X-ray diffraction study showed that amorphous carbon was left as a residue. Low molecular weight fluorocarbons were evolved in the reaction.

Kuriakose and Margrave<sup>33</sup> have decomposed samples of CF<sub>x</sub> at temperatures from 420 to 580 °C and analyzed the gaseous products in a time-of-flight mass spectrometer. They found that the products consisted of perfluoroparaffins, tetrafluoroethylene, and two series of polyunsaturated compounds with general formulas C<sub>n</sub>F<sub>n+4</sub> and C<sub>n</sub>F<sub>n+3</sub> where  $n \geq 3$ , for even and odd numbers of carbon atoms, respectively. Polyolefinic fluorocarbons with up to 22 carbon atoms were detected.

Recently, Kamarchik and Margrave<sup>34</sup> have employed extensive isothermal thermogravimetric analyses to obtain kinetic data on this decomposition. Experiments were conducted with CF<sub>x</sub> samples ranging in stoichiometry from CF<sub>0.61</sub> to CF<sub>1.12</sub> in the temperature range 450 to 650 °C and in both vacuum and nitrogen atmospheres. X-ray diffraction patterns and elemental analyses of the solid residues as well as matrix-isolation infrared spectra of the gaseous products were used to supplement the kinetic data in formulating a detailed decomposition scheme.

The kinetic data were fit to the Avrami-Erofeyev equation<sup>35</sup>

$$-\ln(1 - \alpha) = (kt)^n$$

where  $k$  is an apparent rate constant and  $n$  is a constant which depends on the dimensionality of growth along the reactant-product interface. The value  $n = 2$  has been shown to give the best fit to the data, and Avrami<sup>35</sup> has shown that this corresponds to a situation where the kinetics of two-dimensional growth of nuclei are governed by the growth rate of nuclei and not their rate of formation. Considering the layered structure of CF<sub>x</sub>, a two-dimensional growth of product-reactant interface seems quite reasonable.

Activation energies were calculated by a consideration of the temperature variation of the apparent rate constant and are presented in Table V. No systematic dependence on stoichiometry was observed. It was noted that the less highly fluorinated samples were less thermally stable; however, the activation energies do not account for this observation. An alternative explanation is that the less highly fluorinated samples have larger numbers of atoms other than fluorine bonded at the edge sites (presumably oxygen and

Table V  
Activation Energies of CF<sub>x</sub> Decomposition

Sample	E <sub>a</sub> , kcal/mol
CF <sub>1.12</sub> under nitrogen	50.9 ± 4.2
CF <sub>1.12</sub> under vacuum	61.0 ± 3.4
CF <sub>1.08</sub> under nitrogen	44.8 ± 4.7
CF <sub>0.96</sub> under vacuum	59.4 ± 5.8
CF <sub>0.61</sub> under nitrogen	55.1 ± 4.5

hydrogen), and these weaker bonds are favored nucleation sites.

A consideration of analytical data on the original CF<sub>x</sub> and decomposition residues along with a mass balance calculation has led to the conclusion that C<sub>2</sub>F<sub>4</sub> is the primary gaseous product and that the other gases observed in this work and in the work of Kuriakose and Margrave<sup>33</sup> result from pyrolysis of the C<sub>2</sub>F<sub>4</sub> on the hot walls of the reaction chambers. This information along with the kinetic data leads to the suggestion that the final decomposition step is occurring at the edges of the CF<sub>x</sub> crystallites, where the carbon atoms are already bonded to two fluorine atoms and the only requirement for the production of C<sub>2</sub>F<sub>4</sub> is that two C-C bonds be broken. As C-C bonds are broken, additional F atoms migrate from the interior of the crystallite to the edges, filling the vacant bonding positions on the carbon radicals and resulting in a return to graphite-like C-C multiple bonds in the interior. This is consistent with the kinetic data which favor planar growth of the interface and with X-ray powder diffraction results for the residues which show the presence of graphite.

It has also been observed that as little as 0.5% fluorine in a 1 atm fluorine/nitrogen mixture is sufficient to completely inhibit the decomposition up to 796 °C. This may be explained by identifying C-C, C-O, or C-H bond breakages as the nucleation process. The resulting radical sites would lead to the splitting off of C<sub>2</sub>F<sub>4</sub> groups and propagation of the radical as discussed above. If the nucleation step is very much slower than growth, the radicals produced in this step could be scavenged by fluorine atoms, thus breaking the reaction propagation chain.

In summary, the crystalline CF<sub>x</sub> solids appear to be the most stable fluorocarbons known and should be useful with minimal thermal degradation and/or oxidation in air at temperatures up to 470 °C or in an inert atmosphere, up to 540 °C. In the presence of traces of fluorine, it appears that solid CF<sub>x</sub> might be useful at temperatures as high as 800 °C.

Diamonds which have been treated with fluorine acquire a passivating fluorocarbon coating and then are stabilized against further fluorination up to at least 1000 °C.<sup>36</sup>

This work was supported financially by the National Science Foundation, the U.S. Army Research Office (Durham), the National Aeronautics and Space Administration, and the Robert A. Welch Foundation. Liquid helium was provided under a grant from the Office of Naval Research.

(36) R. B. Badachhape and J. L. Margrave, unpublished work, Rice University.

(33) A. Kuriakose and J. L. Margrave, *Inorg. Chem.*, **4**, 1639 (1965).

(34) P. Kamarchik, Jr., and J. L. Margrave, *J. Thermal Anal.*, **11**, 259 (1977).

(35) M. Avrami, *J. Chem. Phys.*, **8**, 212 (1950).