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A STUDY OF THERMAL DECOMPOSITION OF THE SOLID-LAYERED FLUOROCARBON, POLY(CARBON MONOFLUORIDE)*

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Isothermal-thermogravimetric analyses were used to obtain kinetic data on the CF_x decomposition. Weight of sample *vs.* time curves were obtained for compounds having stoichiometries $CF_{0.61}$, $CF_{0.96}$, $CF_{1.08}$, and $CF_{1.12}$ for several different temperatures over the range 450–650° and in both a nitrogen atmosphere and in vacuum. A small percentage of fluorine in the atmosphere was shown to strongly inhibit thermal decomposition.

These experimental results were fit to various theoretical models and it was found that a satisfactory fit was obtained by use of the Avrami equation, $-\ln(1-\alpha) = (kt)^n$, where α is the extent of reaction, k is an apparent rate constant, and n is an apparent reaction order. The value $n = 2.0$ was indicated which corresponds to planar growth of the decomposed phase.

This information was combined with analytical data for the gaseous and solid products of decomposition to formulate a detailed mechanism.

A series of crystalline fluorocarbons with formulas varying continuously from $CF_{x\simeq 0.0}$ to $CF_{x=1.12}$ have been prepared. The color of this non-stoichiometric compound varies with fluorine content and ranges from black for fluorine/carbon ratios up to about 0.9, to gray from 0.9 to 1.0, to white above 1.0. A grayish product with the composition $CF_{0.92}$ was first prepared by Ruff and Bretschnieder [1] in 1933, by heating graphite, in a stream of fluorine gas, to 420–460.° Later work indicated that the product was of variable composition [2] and depended on reaction temperature, reaction time, and the source of the original graphite.

In this laboratory, the highest fluorine content attained in a high-temperature reaction between gaseous fluorine at one atmosphere and graphite, is quite reproducible and corresponds to a stoichiometry of $CF_{1.12}$. The conditions for preparing this composition of CF_x are a temperature of 627° and at least 1.5 times as many moles of F_2 as moles of carbon.

The difficulties encountered in growing single crystals of CF_x have resulted in ambiguous interpretations of structural data as derived from X-ray powder diffraction [3], solid state NMR [4], and IR spectroscopy. Basically the crystalline structure consists of fused cyclohexane-like carbon rings with fluorine atoms

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occupying the fourth coordination site on each of the sp^3-hybridized carbon atoms. Infrared data have indicated that the number of carbon sites which are doubly fluorinated increases with increasing F/C ratio. Figures 1 and 2 show suggested structures. Lattice dimensions for the "chair" structure are $a_0 = b_0 = 2.53$ Å; $c_0 = 5.76$ Å; $\gamma = 118.8°$; and for the "boat" structure are $a_0 = 2.47$ Å; $b_0 = 4.11$Å; and $c_0 = 5.76$ Å. The question of whether or not the cyclohexane-like rings are all in the "chair" or "boat" configuration or some combination of these is not completely resolved. The possibility of the presence of $F_2^{\delta-}$ or $F_3^{\delta-}$ intercalated between $C_n^{\delta+}$ layers is also still under consideration.

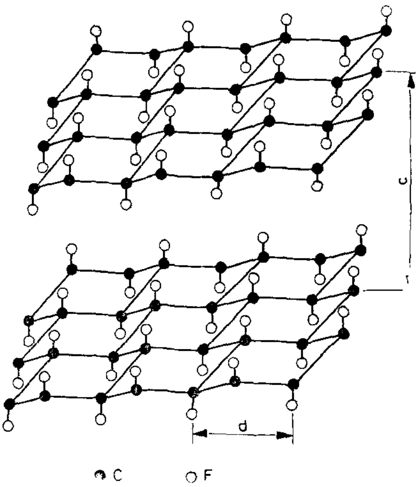

Fig. 1. Structure of "chair" CF_x. *a* and *c* indicate the hexagonal lattice dimensions

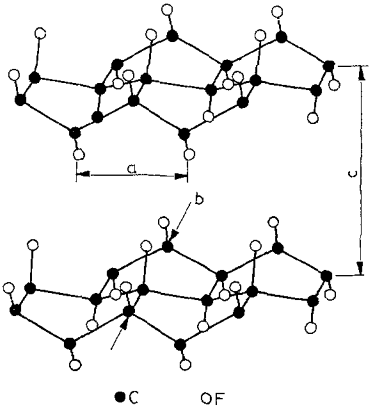

Fig. 2 Structure of "boat" CF_x. *a*, *b* and *c* indicate the orthorhombic lattice dimensions

There has recently been a great deal of interest in CF_x from a practical standpoint. It has been shown to be a superior lubricant [5] under extreme conditions of high temperature and high vacuum. It has also been used quite successfully as a cathodic depolarizer in high energy density batteries [6] and has been used as a gaschromatographic stationary phase [7]. Many of these applications have been hampered by the lack of information about the high temperature reactivity of this compound.

The present studies should also help to elucidate the complex problems encountered in kinetic studies of solid state reactions. The structure of CF_x, a pseudo-two-dimensional crystal, presents an excellent opportunity to test some theoretical models, such as Avrami's model [8] for plate-like growth of product phase.

Experimental

Isothermal-thermogravimetric analyses were carried out using an Ainsworth Type RVA-AU-2 recording micro-balance coupled with a Bristol model 560 strip chart recorder. The samples were contained in an alumina cell and suspended from the balance arm by means of the thermocouple wires. Thermal contact was maintained between a Pt/ 10%Rh-Pt thermocouple and the samples being decomposed. The *EMF* of this thermocouple was monitored by the second pen on the chart recorder to provide a dual trace of weight of sample and temperature as functions of time.

Experiments were carried out in both a nitrogen atmosphere and in a vacuum of less than 10^{-4} torr. Samples of composition $CF_{1.12}$, $CF_{1.08}$, $CF_{0.96}$, and $CF_{0.61}$ were decomposed at several temperatures in the range 450 – 650°. These samples were prepared using Union Carbide SP-2 grade synthetic graphite and Allied Chemicals fluorine which had been passed through a sodium fluoride filled trap to eliminate HF. The preparation followed the procedures described in previous publications [9].

Analyses of the gaseous products were carried out by means of matrix-isolation infrared spectroscopy because of the possibility of producing short-lived, highly reactive species such as CF monomer, difluoroacetylene, or CF_2. In this technique, a CF_x sample was heated in an open-ended furnace inside the vacuum chamber of the matrix apparatus. The evolved gases were directed to a copper surface, which was cooled by liquid helium to about 12 K, where the gases were co-condensed with nitrogen. In this way reactive species were effectively isolated from one another by an inert matrix and could be studied by IR or other spectroscopy. A detailed description of the apparatus has been published [10].

Besides allowing the observation of very reactive species, this technique offers advantages in the identification of stable molecules. At the low temperatures used for the trapping, all molecular rotations except those for a few small hydrides are quenched, which considerably decreases the width of the absorption bands. The extreme sharpness of the bands allows for very accurate measurement of positions and therefore unambiguous identification of the products.

Results and discussion

Kinetics

The data obtained from the thermo-balance are in the form of the weight of the sample plus boat assembly as a function of time. These data were used to calculate "extent of reaction" versus time curves. The extent of reaction was

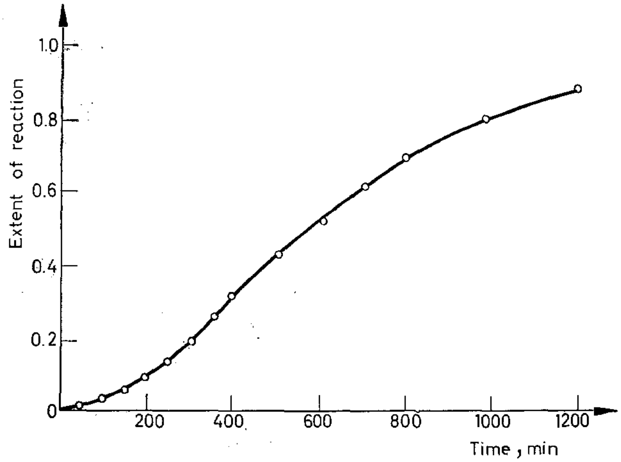

Fig. 3. Decomposition of $CF_{1.12}$ at 565°, under vacuum

Table 1

Maximum decomposition rates for some CF_x samples at selected temperatures

Sample	Atmosphere	Temperature, °C	Maximum* Rate
$CF_{1.12}$	Vac	565	.0013
$CF_{1.12}$	Vac	624	.0130
$CF_{1.12}$	Vac	657	.0452
$CF_{1.12}$	N_2	550	.0012
$CF_{1.12}$	N_2	587	.0037
$CF_{1.12}$	N_2	639	.0411
$CF_{1.08}$	N_2	520	.0014
$CF_{1.08}$	N_2	576	.0045
$CF_{1.08}$	N_2	651	.0705
$CF_{0.96}$	Vac	465	.0006
$CF_{0.96}$	Vac	527	.0078
$CF_{0.96}$	Vac	540	.0183
$CF_{0.61}$	Vac	555	.0281
$CF_{0,61}$	Vac	583	.1125

* Percentage extent of reaction per minute

defined as the fraction obtained by dividing the weight loss at any time by the total weight loss, for that sample in the limit of very long decomposition time:

$$\text{Extent of reaction} = \alpha_t = \frac{W_i - W_t}{W_i - W_f}$$

where α_t is the extent of reaction at time t; W_i is the initial weight; W_t is the weight at time t; and W_f is the final weight. Examples of these curves are shown in Figs 3 and 4. Maximum rates are given in Table 1.

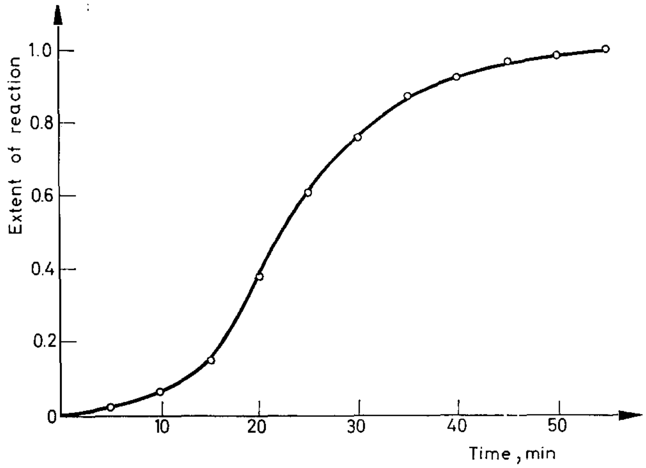

Fig. 4. Decomposition of $CF_{1.12}$ at 657°, under vacuum

These kinetic data were fit to the Avrami–Erofeyev equation [8]

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

where k is an apparent rate constant and n is a constant which depends on the dimensionality of growth along the reactant-product interface.

By plotting $\ln[-\ln(1 - \alpha)]$ *vs.* $\ln t$ and taking the slope of this line, values for the exponent, n, were determined. The value $n = 2$ was indicated this was substituted into the equation.

$$[-\ln(1 - \alpha)]^{1/n} = kt$$

This function was plotted versus time. Examples of these plots are shown in Figs 5, 6 and 7. The good linearity of these plots indicates that $n = 2$ is the correct choice for this exponent.

Avrami [8] has shown that the value $n = 2$ corresponds to either: (1) two dimensional growth of nuclei where the kinetics are governed by the growth of nuclei and not by their formation or (2) one dimensional growth of nuclei where the kinetics are governed by the nucleation process. The former is generally taken as the deceleratory part of two-dimensional-growth kinetic curves and the later as the acceleratory part of one-dimensional-growth kinetic curves. The curves here are therefore taken to be almost wholly deceleratory. This is especially true at the higher temperatures.

Considering the layered structure of CF_x, a two dimensional growth of product-reactant interface seems quite reasonable. The later parts of the curves do not strictly fit the Avrami equation with $n = 2$; however, the rate controlling mecha-

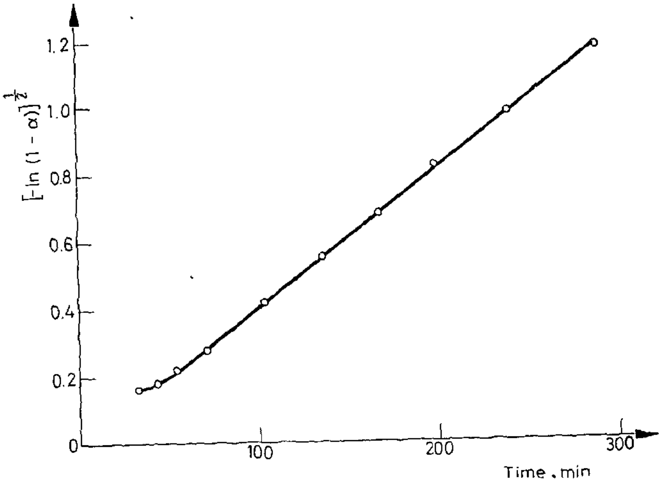

Fig. 5. $[-\ln(1-\alpha)]^{1/2}$ vs. time for $CF_{1.12}$ at 564°, under N_2

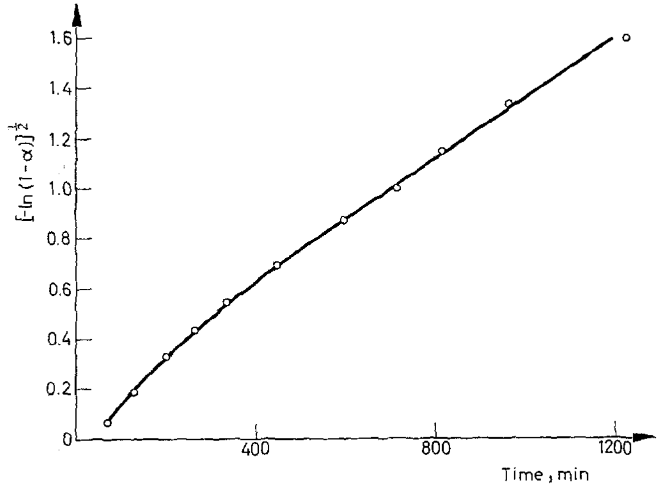

Fig. 6. $[-\ln(1-\alpha)]^{1/2}$ vs. time for $CF_{1.12}$ at 549°, under N_2

nism may be different in the later part of the decomposition as will be discussed in more detail below.

The slopes of the lines in the $[-\ln(1-\alpha)]^{1/n}$ *vs.* t plots are apparent rate constants. These were used to construct Arrhenius plots, examples of which, are shown in Figs 8 and 9. The resulting activation energies are given in Table 2. The physical significance of activation energies obtained in these kinds of calculations is not clearly determined, but they have been shown [11] to give some idea

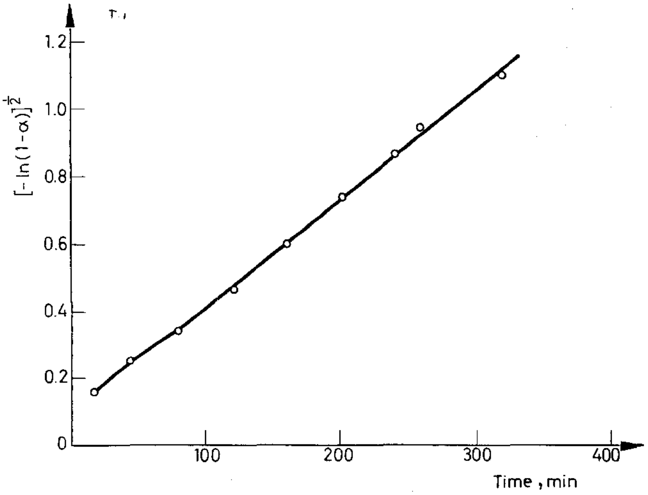

Fig. 7. $[-\ln(1-\alpha)]^{1/2}$ *vs.* time for $CF_{0.96}$ at 506°, under vacuum

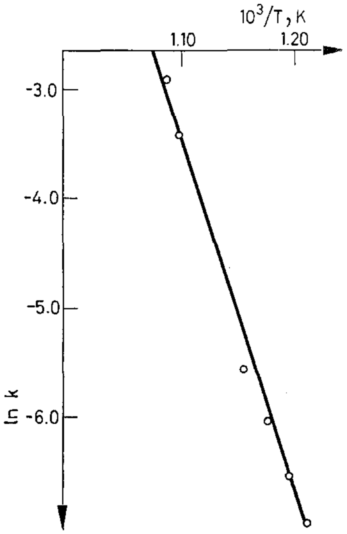

Fig. 8. Arrhenius plot for $CF_{1.12}$ decomposition under vacuum

Table 2

Activation energies of CF_x decomposition

Sample	E_a, kcal/mole
$CF_{1.12}$ in Nitrogen	50.9±4.2
$CF_{1.12}$ in Vacuum	61.0±3.4
$CF_{1.08}$ in Nitrogen	44.8±4.7
$CF_{0.96}$ in Vacuum	59.4±5.8
$CF_{0.61}$ in Nitrogen	55.1±4.5

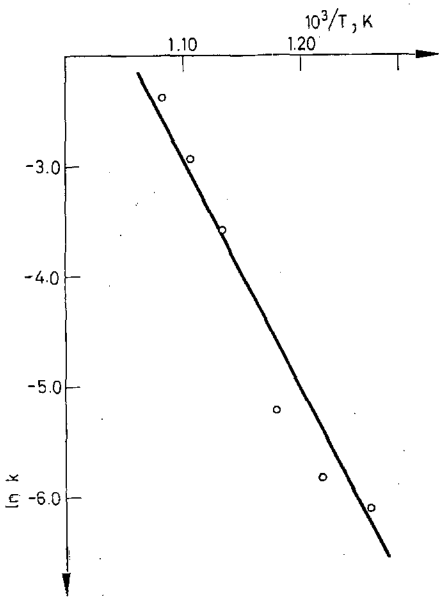

Fig. 9. Arrhenius plot for $CF_{1.08}$ decomposition under N_2

of the energy requirements for reaction. Although there are large uncertainties associated with the activation energies, it can still be seen that there is no systematic dependence of E_a on F/C ratio. It should be noted from Table 1, that those samples with smaller F/C ratios are less thermally stable but the activation energies do not account for this observation. An alternate explanation is that the less highly fluorinated samples have larger numbers of atoms other than fluorine bonded at the edge sites (presumably oxygen and hydrogen) and these weaker bonds are favored nucleation sites.

Matrix IR

The argon-matrix IR spectra of the gaseous products from the decomposition of $CF_{1.12}$, $CF_{1.08}$ and $CF_{0.99}$ were recorded with a wide range of products being observed. The most prominent absorptions were due to CF_4, C_2F_4 and C_2F_6. These products appear in the spectrum of every sample at every temperature tried. In fact very little difference is seen either from one sample to another or from one temperature to another.

Suggested decomposition mechanism

It is possible to use the percent weight loss at completion of decomposition and the *F/C* ratio of the decomposition residue to write balanced equations where the fluorocarbon gases produced are represented by an empirical formula giving the average *F/C* ratio in all the product gases taken collectively. For example at 553° under vacuum:

$$1.89\ CF_{1.12}(\text{solid}) \rightarrow 0.89\ CF_{0.17}(\text{solid}) + CF_{1.97}(\text{gases})$$

The $CF_{1.97}$ represents either the average empirical formula of all the gaseous products or the empirical formula for a single gaseous product if only one is formed. Another example, for a decomposition at 593° is:

$$2.63\ CF_{1.12}(\text{solid}) \rightarrow 1.63\ CF_{0.06}(\text{solid}) + CF_{2.84}(\text{gases})$$

For $CF_{1.97}$ the *F/C* ratio of the gaseous products increase from ~ 2.0 to ~ 2.8 with increasing temperature; however, for $CF_{0.96}$ the equation

$$2.50\ CF_{0.96}(\text{solid}) \rightarrow 1.50\ CF_{0.08}(\text{solid}) + CF_{2\cdot 28}(\text{gases})$$

is approximately obeyed throughout the temperature range used.

The mixture of CF_4, C_2F_4 and C_2F_6 observed in the matrix IR and an average *F/C* ratio for all the product gases of about 2.0 is easily explained by assuming that the only abundant gaseous product is C_2F_4 but at higher temperatures other gases may arise from pyrolysis of the C_2F_4 on the hot walls of the furnace. This pyrolysis would produce the carbon deposits which have been observed on the hot zone of the glass jacket extending below the microbalance and on the furnace of the matrix vacuum chamber along with CF_4 and C_2F_6.

A consideration of these data and the kinetic results which indicated planar growth of nuclei, leads to the suggestion that the final decomposition step is occurring at the edges of the CF_x crystallites, where the carbon atoms are already bonded to two fluorine atoms and the only requirement for the production of C_2F_4 is that two C–C bonds be broken. See Fig. 10. As C–C bonds are broken, additional F atoms migrate from the interior of the crystallite to the edge, 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. Using 95 kcal/mole [11] for the strength of a C−C single bond and 176 kcal/mole as the strength of the $F_2C=CF_2$ bonds, a ΔH of +89 kcal/mole can be calculated for loss of C_2F_4. Because of the large spread in calculated activation energies, it is impossible to conclusively identify this process as the rate controlling one. In fact, because of the greater energy of the C−F bond, fluorine migration may be rate controlling. The poorer fit of the Avrami equation with $n = 2$ in the later part of the decomposition may indicate that the kinetics have changed from being controlled by the rate of growth of nuclei to being controlled by the rate of diffusion-supplied fluorine atoms.

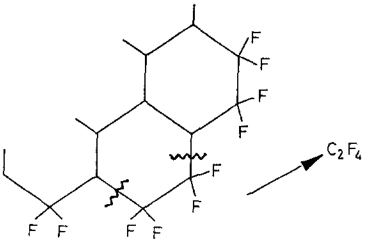

Fig. 10. Bond breakage scheme for CF_x decomposition

It has also been observed that, as little as 0.5% fluorine in a one atmosphere fluorine/nitrogen mixture, is sufficient to completely inhibit the decomposition up to 795°. 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_2F_4 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. Since any weight change as a result of this reaction would depend on the nucleation rate, no change would be observed over the times used in these experiments.

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References

1. O. Ruff, O. Bretschneider and F. Ebert, Z. Anorg. Allgem. Chem., 217 (1934) 1.
2. a. W. Rudorff and G. Rudorff, Z. Anorg. Allgem. Chem., 253 (1974) 281.
   b. W. Rudorff and G. Rudorff, Chem. Ber. 80 (1947) 413.
   c. W. Rudorff, in Handbook of Preparative Inorganic Chemistry, Vol. 1, (G. Brawer, ed.), Academic Press, New York, 1963, p. 635.
   d. W. Rudorff, Adv. Inorg. Chem. and Radiochem., 1 (1959) 223.

3. V. K. MAHAJAN, R. B. BADACHHAPE, and J. L. MARGRAVE, Inorg. and Nuclear Chem. Lett., 1103 (1974) 10.

4. L. B. EBERT Ph. D. Thesis, Chemistry Department, Stanford University, Stanford, California, 94204, Chapter VIII, 1975.

5a. R. L. FUSARO and H. E. SLINEY, Graphite Fluoride: A New Solid Lubricant, NASA Technical Memorandum, NASA TM X-52624, 1969.

b. R. L. FUSARO and H. E. SLINEY, Graphite as a solid Lubricant in a Polyimide Binder, Lewis Research Center Technical Report, 1971.

c. H. GISSER, M. PETRONIO, and A. SHAPIRO, J. Amer. Soc. Lub. Engs., 28 (1972) 161.

6a. N. WATANABE and M. TAKASHIMA, Proceedings of the 7th International Symposium on Fluorine Chem., Santa Cruz, California, July, 1973.

b. N. WATANABE, et al., J. Electrochem. Soc. Japan, 32 (1964) 17.

c. H. F. HUNGER and G. J. HEYMACH, J. Electrochem. Soc., 120 (1973) 1161.

7. L. C. SWOPE and E. A. SMITH, U.S. Patent No. 3,877,894, April 15, 1975.

8. M. AVRAMI, J. Chem. Phys., 8 (1940) 212.

9a. R. J. LAGOW, R. B. BADACHHAPE, J. L. WOOD, and J. L. MARGRAVE, J. C. S. Dalton, 1974 (1974) 1268.

b. PETER KAMARCHIK JR., Ph. D. Thesis, Chemistry Department, William Marsh Rice University, Houston, Texas, 77001, May 1976.

10. Z. H. K. ISMAIL, Ph. D. Thesis, Chemistry Department, William Marsh Rice University, Houston, Texas, 77001, 1972.

11. J. ZSAKO and CS. VARHELYI, J. Thermal Anal. 7 (1975) 33.

12. F. P. LOSSING, private communication to V. H. Dibeler of the Mass Spec. Section, Nat. Bureau of Standards, Washington, D. C.

RÉSUMÉ — La TG isotherme a été utilisée pour obtenir des données cinétiques sur la décomposition de CF_x. Les courbes donnant le poids de l'échantillon en fonction du temps ont été energistrées à différentes températures, entre 450 et 650°, en atmosphère d'azote et sous vide, sur des composés de composition $CF_{0.61}$, $CF_{0.96}$ et $CF_{1.08}$. Un faible pourcentage de fluor dans l'atmosphèere s'est avéré inhiber considérablement la décomposition thermique.

Ces résultats expérimentaux ont été confrontés à divers modèles mathématiques. On a trouvé un ajustement satisfaisant à l'aide de l'équation d'Avrami, $-\ln(1-\alpha) = (kt)^n$, où α es l'avancement de la réaction, k une constante de vitesse apparente et n un ordre de réaction apparent. La valeur $n = 2.0$ correspond à une croissance dans le plan de la phase décomposée.

Cette information a été combinée avec des données analytiques sur les produits de décomposition gazeux et solides, afin de formuler un mécanisme détaillé.

ZUSAMMENFASSUNG — Isotherm-thermogravimetrische Analysen wurden durchgeführt um kinetische Daten über die Zersetzung von CF_x zu erhalten. Probengewicht—Zeit-Kurven wurden für Verbindungen mit stöchiometrischen Verhältnissen von $CF_{0.61}$, $CF_{0.96}$, $CF_{1.08}$ und $CF_{1.12}$ bei verschiedenen Temperaturen im Bereich von 450° bis 650°, in Stickstoff sowie im Vakuum aufgenommen. Ein geringer Prozentsatz an Fluor in der Atmosphäre wirkte stark inhibierend auf die thermische Zersetzung.

Diese Versuchsergebnisse wurden verschiedenen theoretischen Modellen angepasst und es wurde gezeigt, dass mit Hilfe der Avrami-Gleichung $-\ln(1-\alpha) = (kt)^n$ eine befriedigende Anpassung möglich ist, wobei α = Ausmaß der Reaktion, k = scheinbare Geschwindigkeitskonstante und n = scheinbare Reaktionsordnung ist. Der angedeutete Wert $n = 2.0$ entspricht einer planaren Zunahme der zersetzten Phasen.

Diese Information wurde mit analytischen Daten der gasförmungen und festen Zersetzungsprodukte kombiniert um einen Mechanismus in allen Einzelheiten zu formulieren.

Резюме — Изотермический-термогравиметрический анализы были использованы для получения кинетических данных по разложению CF_x. Были получены кривые в координатах вес образца — время для соединений стехиометрического состава $CF_{0.61}$, $CF_{0.96}$, $CF_{1.08}$ и $CF_{1.12}$ при нескольких различных температурах в области 450°—650°, как в атмосфере азота, так и в вакууме. Небольшое процентное содержание фтора в атмосфере сильно подавляет термическое разложение. Экспериментальные результаты были подставлены в различные теоретические модели и было найдено, что удовлетворительное соответствие получено при использовании уравнения Аврами $-\ln(1-\alpha) = (kt)^n$, где α — степень реакции, k — кажущаяся константа скорости, а n — каждущийся порядок реакции. Указано значение $n = 2$, которое соответствует планарному росту фазы разложения. Полученная информация объединена с аналитическими данными по газообразным и твердым продуктам разложения, чтобы сформулировать детальный механизм.