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CHAPTER 12

Fluorocarbons and Their Production

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Introduction

The fluorocarbons are destined to become a new and very large domain of chemistry. They can be expected in the not too distant future to rival that branch of chemistry called organic. As their name implies, they are compounds of fluorine and carbon; but in a more restricted sense they are compounds, analogous to hydrocarbons, with fluorine atoms occupying the positions of hydrogen atoms in hydrocarbons. Chemically, however, the properties of these compounds are so vastly different from their hydrogen-containing analogs that entirely new and different techniques, methods of synthesis, and reactions are necessary.

Hydrocarbons and their derivatives, i.e., organic chemical compounds, are extremely useful for mankind, these uses being chiefly in two important areas. They are very reactive substances which are particularly susceptible toward oxidation. For this reason they are extensively used for fuel and for food. Oxidation is without question the most important organic chemical reaction. The other area in which organic compounds are useful is as materials of construction such as wood, paint, lubricants, fabrics, plastics, and rubber. Here this ease of combustion is highly disadvantageous. Slow oxidation causes deterioration as in paint, dyes, and rubber; and rapid oxidation causes tremendous destruction of life and property in fires.

The fluorocarbons and their derivatives appear destined to fill th
role of "materials of construction" completely free from the ravage
of either slow or rapid oxidation, so in this area they should be greatl
superior to organic chemical substances. Most organic compounds ar
subject to gradual deterioration by slow oxidation, but the fluorocarbon
are free from this defect. For the same reason bacterial life and insec
cannot use fluorocarbon material for food, and substances made from o
protected by fluorocarbons are free from decay and insect damage
Fluorocarbons are completely nonorganic, when it comes to being eithe
used or produced by organisms. In addition to being completely non
combustible, the fluorocarbons are resistant to the action of chemica
agents, including the strong acids and bases and strong oxidizing an
reducing agents.

TABLE I

Bond Energies
kcal./mol.

	F	Cl	Br	I	H	C	Bond radii
F	63.5	86.4			147.5	107.0	0.64
Cl	86.4	57.8	52.7	51.0	102.7	66.5	0.99
Br		52.7	46.1	42.9	87.3	54.0	1.14
I		51.0	42.9	36.2	71.4	45.5	1.33
H	147.5	102.7	87.3	71.4	103.4	87.3	0.30
C	107.0	66.5	54.0	45.5	87.3	58.6	0.77

Prior to the first identification of liquid fluorocarbons in 1937 (21), i
was not considered feasible to create molecules of carbon and haloger
alone containing more than three carbon atoms per molecule. C_3Cl
had been prepared and found to be high melting and not very stable
No higher members of this series had been identified. The commor
fallacy of analogy led to the expectancy of instability for higher molecula
weight compounds of carbon and halogen. Now that numerous com
pounds in the fluorocarbon domain have been prepared and studied, w
are forceably brought to the realization that analogy between chlorin
and fluorine in chemical compounds is extremely hazardous and tha
between organic compounds and fluorocarbon compounds even more so
Once it was demonstrated (22) that fluorocarbons containing mor
than three carbon atoms per molecule were extremely stable and unreac
tive substances, it was very easy to rationalize these properties, surprisin
as they were at that time. Considering the fundamental properties o
bond energies and bond radii (12) shown in Table I, it is easy to see tha
fluorine atoms are held more firmly to the carbon skeleton than are th

atoms of any other element. There is an additional factor which the bond radii indicate but do not adequately express. Hydrogen atoms surrounding the carbon skeleton in hydrocarbons in the tetrahedral arrangement do not completely cover and protect the carbon atom or the bonds between atoms. A complete shell of chlorine atoms surrounding a carbon skeleton exists under strains and repulsive forces as the chlorine atoms are too large for the symmetrical, stable structure. A complete covering of fluorine atoms over the carbon skeleton apparently form a sufficiently compact envelope so as to protect both the carbon atoms and the bonds (or internal force fields) from exposure or attack from outside molecules, without at the same time creating undue internal repulsions. Most chemical reactions of carbonaceous structures involve attack either at an exposed carbon atom, as in the back side entrance in the Walden inversion or at exposed bonds or force fields. The compact fluorine atom envelope in the fluorocarbons forms such a protective coating that the rate of reaction is greatly reduced even under conditions where reactions are allowed or favored by thermodynamics. Thus it can be truly stated that fluorocarbons have hearts of diamond and skins of rhinoceros hide.

As the fluorocarbons and their derivatives are both much more stable thermodynamically and more resistant structurally to chemical attack than analogous organic compounds, it can be expected that not only can most of the structures of organic chemistry be duplicated in the fluorocarbon domain but also many compounds not feasible in organic chemistry can be obtained as stable substances. This will permit the creation of a greater number of compounds in the fluorocarbon domain than in organic chemistry. The number of compounds that will be prepared that are part fluorocarbon and part organic becomes enormous, so much so that our present systems of classifying and arranging will probably not be satisfactory.

There are differences between fluorocarbon compounds and organic compounds that do not permit completely analogous structures in the two domains. Compounds containing the grouping R—OH where R is fluorocarbon will not be very stable because of the ready formation of HF. However, this is counterbalanced by the fact that R—OF is stable in the fluorocarbon domain but is not in organic chemistry. CF_3OF and CH_3OH are stable but not CF_3OH or CH_3OF. A similar situation may exist for most amines although one fluorocarbon compound of this type is known $(CF_3)_2NH$. Compounds of the types RNF_2 and R_2NF (derivatives of nitrogen trifluoride) are quite stable substances in the fluorocarbon domain but unknown in organic chemistry. Dimethforyl peroxide, CF_3OOCF_3, has none of the explosive instability of dimethyl peroxide. Similarly higher oxidized types of other kinds will be found

stable in the fluorocarbon domain that do not exist in the organic do
or are unstable in it.

Fluorocarbon Nomenclature*

With a new field of chemistry of tremendous magnitude and in
tance in its infancy, just beginning to be recognized, and on the
of an explosive expansion, it is well to pause and consider the lang
that will be used in it. We will be guilty of misusing our trust by in
ing an outmoded, cumbersome, and inappropriate system of nome
ture on an important branch of chemistry in the future, if tradition
the forms and prejudices of some other branch of chemistry are perm
to influence the selection of names. The English system of weight
measures is continued despite its cumbersomeness and tremendous
because of inertia and fear of temporary inconvenience. We wi
saddled with a system of nomenclature as archaic as the English sy
of weights and measures, if we fail at this time to adopt a system
on the fluorocarbons and for the fluorocarbons. This is an opport
that is available now as the field is just in its infancy, but this is
responsibility and a challenge. Fluorocarbons are not hydroca
nor derivatives of hydrocarbons, and no system of naming which cla
them as such would conceivably be satisfactory. To do this wou
equivalent to requiring all compounds of an element to be nam
derivatives of the hydrides of that element. Must we call tabl
perchlorosodium hydride? Is quartz peroxysilane? Is borax a d
tive of diborane? Must sulfuric acid be named as a derivative of h
gen sulfide, and nitric acid one of ammonia? These are no
ridiculous than calling fluorocarbons—perfluorohydrocarbons.
fluorocarbons will be more numerous than the hydrocarbons, an
system of naming the fluorocarbons and their derivatives which pres
the hydrocarbon names intact can be anything less than a device fo
jugating the fluorocarbons to the unwarranted status of derivativ
hydrocarbons.

* As this book goes to press there has been some discussion but no final d
as to an adequate nomenclature for use in the fluorocarbon system. Considera
being given to a set of names based upon hydrocarbon names with the prefix pe
before the hydrocarbon name. It appears now that this would result in great
to the future of the science of chemistry. First, the syllable "per" has
important uses in inorganic chemistry which would lend confusion. Second,
syllable "per" will be needed for fluorocarbon peroxides $(CF_3O_2CF_3)$, per
(CF_3CO_3H), and perfluorides $(C_5H_5NF_2)$, it would be used under two or more
tions in the same word for the same chemical. Third, as the hydrocarbon
are retained intact, the system can be nothing but cumbersome, ambiguou
unsatisfactory.

The names of chemical substances are more than mere designations of the association of atoms and their arrangement. To the chemist the name carries connotations of properties and sometimes methods of synthesis and reaction. When a substance is called an acid, it signifies more to the chemist than that the compound contains hydrogen in a specific arrangement. He associated acidic properties with the name. Recently when the first fluorocarbon oxide was identified, it was named an ether from structural reasons. Immediately the name "ether" brought association of a certain set of properties characteristic of hydrocarbon ethers. Physical properties showed these characteristic properties lacking, but the highly efficient chemist measuring these properties was so swayed by the name "ether" that he badly misinterpreted his own measurements. Hydrocarbon names carry certain connotations of properties as well as reactions. As the fluorocarbons lack these properties and do not undergo these reactions, naming the fluorocarbons as derivatives of hydrocarbons will be very misleading as well as very cumbersome. The fact that both the International Union of Chemistry and Chemical Abstracts hydrocarbon derivative nomenclature is cumbersome for fluorocarbons is well recognized by all who have given thought to the matter.

The vital necessity of a distinctive fluorocarbon nomenclature is strikingly emphasized by consideration of mixed types, i.e., part fluorocarbons and part hydrocarbons. A simple example is "perfluoroethyl benzene." Which is this—$C_2F_5C_6H_5$ or $C_2F_6C_6F_6$? More complicated molecules give greater ambiguities.

Another reason for the necessity of a system of naming the fluorocarbons and their derivatives as a separate classification and not as derivatives of hydrocarbons is the importance of separate indexing of a field potentially larger than organic chemistry. This is quite important as can be seen in the relatively minor confusion resulting from the indexing of hydrogen fluoride under hydrofluoric acid.

Whereas a separate and distinct nomenclature for the fluorocarbon field of chemistry is urgently required, it is desirable to use as much as possible of well-known systems and devices so as to impose as little new memory material as can achieve the desired purposes. It is believed that as much as possible of the beautiful systematic structure of organic chemistry is incorporated in the device for naming the fluorocarbons proposed in the first paper so naming this class of compounds (21). The syllable "fluor" was placed before the final syllable in an otherwise organic chemical name for the same structure. A slightly objectional feature was pointed out that a few names so constructed duplicated names of minor hydrocarbons. This objection is overcome by contract-

ing the syllable to "for." This also greatly improves the sounding the names. This system has been proposed (19), and although obje tions to it were requested, none has been received. This system h correspondingly been adopted for this book—methforane (CF_4)— methforyl $(CF_3—)$—ethforane (C_2F_6)—ethforene (C_2F_4)—methfor peroxide $(CF_3)_2O_2$, etc.

Early History

Chemists have been interested in the great reactivity of fluorine from the time Moissan isolated the element and have known its power o igniting carbonaceous substances at room temperature or below. Mois san himself found that carbon and organic substances caught fire in fluorine. He made efforts to isolate the products of the reaction, but hi characterization of these was vague; there was an error of over 110° in the boiling point of methforane. As these reactions are extremely violent, it is not surprising that pure methforane was not prepared unt 1926 (8). Subsequently the reaction between fluorine and carbon was studied more intensively. Products from the high-temperature reac tion between fluorine and wood charcoal in a hard glass tube were par tially identified (17). These were found to be CF_4, SiF_4, CO_2; an indefinite condensate boiling $-50°$ to $-20°C$ with varying molecular weight; and a heavy pleasant smelling fluid boiling over $0°$ contaminated with HF and H_2SiF_6. The authors state that this liquid probably con tained C_2F_6, C_3F_8, and other compounds up to C_6F_{12}, although no sub stances were isolated or identified. Obviously ethforane and propforane must have been in small amounts because of their low boiling points; and the odor must have come from some substance other than the mentioned fluorocarbons, which are odorless. Further work (16) explained the frequency of violent explosions that occur when fluorine is brought in contact with carbon. A white crystalline material is formed that has the composition CF. This material explodes on heating to give chiefly methforane. Because of the violence of the explosions only very small quantities of product could be obtained. Active carbon adsorbed fluorine to form CF below 280°, above 280° and below some tempera tures above 450° explosions result. Only at very high temperatures does the reaction proceed without explosion. With graphite adsorption proceeds below 420°, explosions between 420° and 700°, and no free burning under 700°. A product from the explosive decomposition that is an oily liquid at room temperature is assumed to be C_4F_{10} or at least to average this composition. As neither butforane nor any higher-boiling liquid fluorocarbons had yet been isolated, this assumption is excusable,

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as it was not then known that these were nonoily liquids of low viscosity and that butforane boiled below room temperature.

Ethforane was first obtained from the uncatalyzed reaction between fluorine and carbon (17). This substance was obtained by the electrolysis of acetforic acid in aqueous solution (26) and also by the passage of methforane and difluorochloromethane through an electric arc (15, 27). Ethforene was also first obtained in this manner.

The Catalyzed Reaction between Fluorine and Carbon

A fortunate accident enabled the reaction between fluorine and carbon to be conducted without explosions at a temperature sufficiently low so that a mixture of liquid fluorocarbons was obtained (21). This enabled the isolation of propforane, butforane, pentforane, and hexforane. The quantities obtained from the first set of experiments were insufficient for precise determination of physical properties. It was found that mercury was a good catalyst for the reaction and enabled it to proceed smoothly without explosions and with the formation of significant proportions of fluorocarbons boiling higher than methforane. The first use of the catalyst occurred when an amalgamated copper tube was inadvertently used for the reaction. It was later found that a small amount of any mercury compound added to the carbon served as catalyst (22). The products of the reaction on separation showed 54.5% methforane, 12.6% ethforane, 8.2% propforane, two butforane fractions of 5.3 and 1.3%, 5.5% cyclic C_5F_{10}, 4.4% cyclic C_6F_{12}, 1.3% C_7F_{14}, 5.5% of a mixture boiling 25° to 95°, and 1.5% of a mixture boiling 95° to 160°.

The original isolation and identification of stable fluorocarbons containing four and more carbon atoms per molecule immediately strongly indicated that an entire new field of chemistry would eventually result as further studies were made. This was expressed in the original publication as follows:

"The substances are colorless and either odorless or very nearly so. They are very stable chemically. Many of the tubes containing these were sealed off while an appreciable pressure of the vapor existed inside. No trace of etching or carbonization could be observed in the Pyrex glass seal, which must have been at least 700°. The different fractions were tested for unsaturation with bromine in carbon tetrachloride solution, and no decolorization could be observed.

The formation of stable compounds of carbon and fluorine containing more than three carbon atoms per molecule indicates the possibility of the synthesis of a large number of similar compounds provided that methods can be discovered. Such compounds should be of considerable interest both theoretically and as useful substances.

To indicate the relatively low attractive force between the molecules of these compounds, a graph is shown in the figure. The molecular weight is plotted against the boiling point. On the same graph are represented the inert gases, the hydrocar-

bons, and a few other substances. The fluorocarbon curve does not lie greatly above the inert gas curve, whereas the hydrocarbon curve is very much higher. The fluorocarbons approach the inert gases in properties more closely than any other compounds."
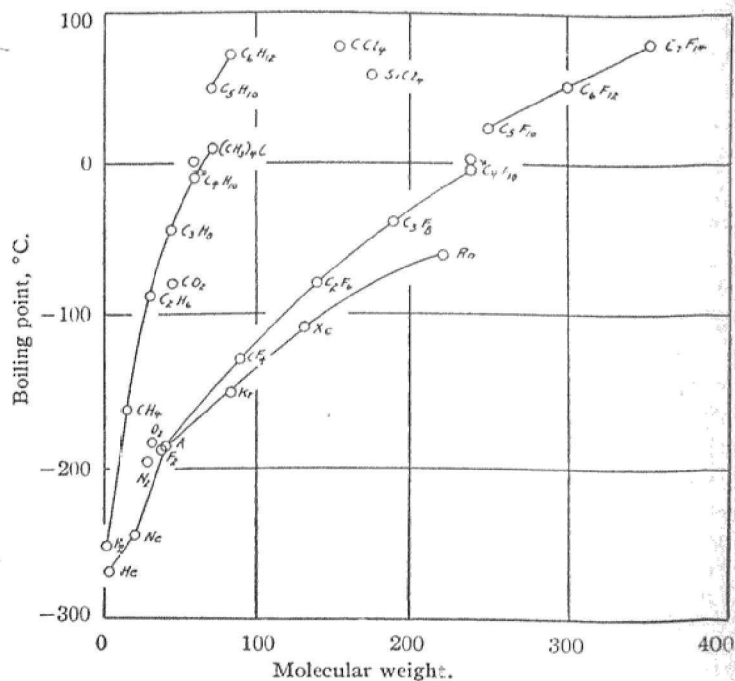

FIG. 1.—Simons and Block comparison of fluorocarbons and other substances.

Recent History

Other methods of obtaining fluorocarbons soon followed. Fredenhagen and Cadenbach (5) controlled reactions between elementary fluorine and liquid hydrocarbons by the beneficial geometry of fine mesh copper screening. No fluorocarbons were produced, but complex products containing a small percentage of fluorine were obtained. Miller, Calfee, and Bigelow (9) employed the same idea for the partial replacement of the chlorine of hexachloroethane with fluorine in the vapor phase. Employing the same technique Young, Fukuhara, and Bigelow (28) fluorinated ethane and obtained some ethforane. It was not until Fukuhara and Bigelow (6) tried benzene that this technique yielded higher molecular weight fluorocarbons. Cady and associates (2) improved this technique by silver plating the copper gauze to provide a catalytic surface in addition to the advantages of geometry provided previously

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and made the production of specific fluorocarbons more feasible by this method. Ruff (13) and Ruff and Ascher (14) showed the preparation of cobaltic fluoride from cobaltous fluoride and fluorine. Fisher and Jaenckner (3) used it in the synthesis of sulfur fluorides. Ruff and Keim (18) used it in the replacement of chlorine with fluorine in carbon tetrachloride. Cobaltic fluoride is a powerful fluorinating agent and is reduced to cobaltous fluoride in the reaction. It is reoxidized back to the cobaltic state by elementary fluorine. Fowler and associates (4) employed this technique with hydrocarbons and prepared large quantities of fluorocarbons. Good yields of specific products are produced by this process. Another interesting method of producing fluorocarbons has been reported by Park and associates (11). From chloroform, CF_2ClH is made, using the Swarts reaction. A thermal decomposition of this material yields in addition to ethforene, small amounts of a compound C_3F_6 (first reported to be cyclopropforane, but now shown to be propforene), cyclobutforane, and compounds of the formula $H(CF_2)_xCl$ (with x extending to 14). These compounds can be chlorinated to replace the hydrogen atom; and then by exhaustive and vigorous fluorination, the chlorine replaced with fluorine. Straight chain and certain cyclic fluorocarbons can be obtained by this path.

Another interesting method of producing fluorocarbons is reported by Miller and associates (10). Elementary fluorine reacts with a completely halogenated olefin in the liquid phase at low temperature to cause coupling in addition to removal of unsaturation by addition of fluorine. An interesting example is the addition of fluorine to $CFCl=CFCl$. In addition to other products $CF_2Cl-CFCl-CFCl-CF_2Cl$ is obtained. Dechlorination yielded $CF_2=CF-CF=CF_2$, butafordiene. On further liquid phase fluorination of this diolefin, fluorocarbons such as C_8F_{18} and $C_{12}F_{26}$ were obtained.

Catalyzed Fluorine and Carbon Reaction—Pilot Plant Study

INTRODUCTION

The AgF_2 catalyzed reaction between fluorine and hydrocarbons and the CoF_3 reaction with hydrocarbons were developed to high efficiency during the period 1942–45 and are described fully elsewhere in this book. Relatively high yields of one specifically desired substance can be obtained with them. As both of these processes use elementary fluorine to replace combined hydrogen, the maximum yield based on fluorine is only 50%, as half of the fluorine goes into the formation of hydrogen fluoride. For wartime purposes costs were not vital and specific products were urgently needed, and these processes were selected over the catalyzed reaction

between fluorine and carbon. In this latter process all the fluorine finds its way into fluorocarbons, but the largest percentage is methforane for which there was little wartime use. As all the fluorocarbons show promising peacetime uses, even to some applications for methforane, the catalyzed reaction between fluorine and carbon has been studied in greater detail. As this process requires much less equipment than other methods of making fluorocarbons and as the recent study shows only 34% methforane, it offers promise of economic advantages over other processes. As this pilot plant study of this process is not elsewhere reported, it is given here in some detail.*

TECHNIQUE

In Fig. 2 is shown the reaction vessel. The charge of carbon and catalyst were placed upon the iron tray. The fluorine was supplied
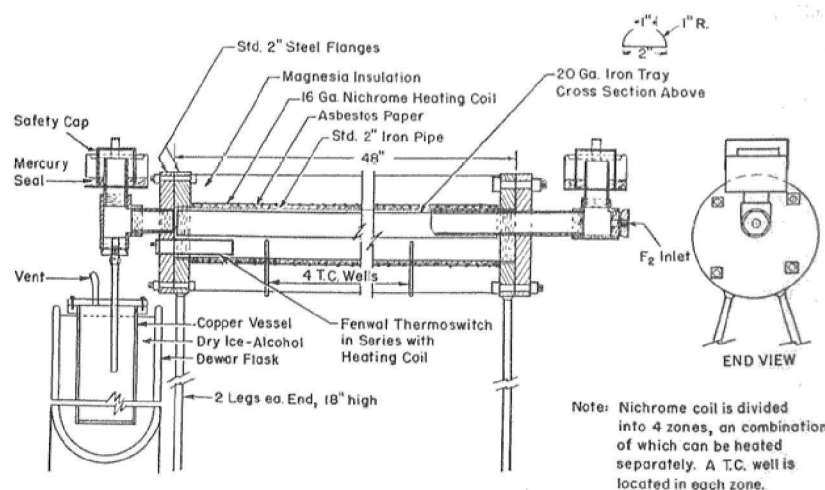

FIG. 2.—Apparatus used in the mercury catalyzed reaction between fluorine and carbon.

from a 50–70 ampere generator, and operation was continuous except for replacement of carbon. As the reaction zone proceeded through the vessel in a relatively narrow region starting at the fluorine entrance, its presence toward the far end of the tube could be detected by the thermocouples. Time for recharge is indicated by the reaction zone reaching the far end of the charge. Each charge consisted of 250 g. of Norit

* The large-scale reaction for fluorocarbon production was conducted in the laboratories of the Minnesota Mining and Manufacturing Company. The separations and identifications were made by Dr. W. H. Pearlson in the author's laboratory under the sponsorship of the above-mentioned company.

carbon mixed with 5% of mercuric fluoride. The temperature of the reaction vessel was held between 350° and 385°.

Although mercury was used as the catalyst in this preparation, it has been found that other substances have catalytic effects on this reaction. Aluminum, antimony, and iron are examples of such catalysts, but they are inferior to mercury under the conditions here employed. Other substances have detrimental effects. Sodium bromide appears to promote the increased production of $(CF)_n$.

PRODUCTS

A total of 19 kg. of fluorocarbons was produced. Separations were made chiefly by distillation, but fractional crystallization was employed in some cases. Fluorocarbons are exceptionally easy and satisfactory substances to distill. Their extremely low surface tension and high density, coupled with a viscosity of the same order as hydrocarbons of

TABLE II

Pattern of Products from the Mercury Catalyzed Reaction of Fluorine and Carbon

Boiling range, °C	Weight %	Carbon atoms per molecule
Below −100	34	C_1
−100 to −75	16	C_2
−75 to −30	14	C_3
−30 to +5	8	C_4
+5 to 42	8	C_5
42 to 57	8	C_6
57 to 80	3	C_7
80 to 110	1.0	C_8
110 to 120	0.6	C_9
120 to 148	0.9	C_{10}
148 to 193	0.4	C_{10}–C_{13}
195 to 239	0.3	C_{13}–C_{16}
Solid at 25°	0.2	C_{16} and higher

the same boiling range, enable satisfactory use of columns of high efficiency with remarkably large through-put. Columns were used having a bore of 9 mm. packed 16 in. with $\frac{3}{64}$ in. stainless steel helices at take-off rates of 2 g. per hour with 50 to 1 reflux ratio. The primary distillation resulted in the separation of products according to the number of carbon atoms up to and including C_{10}. Fractions C_5 and upward each contained a number of isomers and mixtures of cyclic and acyclic compounds. The pattern of products is shown in Table II.

TABLE III

Properties of Fluorocarbons from Fluorine and Carbon Catalyzed Reaction

	Boiling point °C	Freezing point °C	Molecular weight		% F		Liquid density g./cc. at 20°	Refractive index n_D^{20}	Surface tension dynes per cm. 20°	Kinematic viscosity centistokes		Dielectric constant
			Exp.	Calc.	Exp.	Calc.				18°C	37.8°C	
C_5F_{10}	21–22	9.9 to 10.2	249	250	76.0	76.0	1.648	—	11.3	—	—	—
C_5F_{12}	28–29	—	288	288	77.6	79.3	1.634	—	10.2	—	—	—
C_6F_{12} (a)	47.1	−47 to −44	304	300	76.0	76.0	1.723	1.268	12.4	—	—	—
C_6F_{12} (b)	sublimes	51 to 54	300	300	76.0	76.0	—	—	—	—	—	—
C_6F_{14}	55.1–56.1	< −78	342	338	78.4	78.7	1.697	1.256	15.9	1.08	0.76	1.84
C_8F_{16}	97.9–98.9	—	404	400	75.5	76.0	1.841	1.292	14.9	0.73	0.55	—
C_8F_{18}	101.7–102.1	—	437	438	77.1	78.1	1.802	1.282	17.5	2.19	1.39	1.74
C_9F_{16}	115.5–116.0	—	416	412	74.4	73.8	1.884	1.3047	16.7	1.42	1.07	1.76
C_9F_{18}	119.1–123.3	—	455	450	75.8	76.0	1.865	1.294	17.9	2.25	1.47	1.78
$C_{10}F_{18}$ (a)	137.9–139.0	—	466	462	—	—	1.908	1.3077	18.3	—	—	1.79
$C_{10}F_{18}$ (b)	139.5–139.9	—	475	462	75.4	74.2	1.917	1.3088	19.1	4.93	2.73	1.88
C_{12}–C_{13}	171.0–173.0	—	578	574	73.6	—	1.954	1.3212	—	—	—	1.85
$C_{12}F_{22}$	196.0–198.0	> 30	580	—	—	—	—	1.333[a]	—	—	—	—
C_{15-16}	220.0–240.0	—	691	—	—	—	2.039	1.3120	21.6	—	9.85	—
C_{16}?	240.0–250.0	> 30	743	—	—	—	—	—	—	—	—	—
C_{20-22}	280.0–300.0	> 30	850	—	—	—	—	—	—	—	—	—

[a] Supercooled.

A careful redistillation was made of all fractions. The C_5F_{10} fraction was further purified by fractional crystallization, and fractional crystallization combined with distillation separated two isomeric cyclic compounds of the formula C_5F_{12}. The material C_5F_{10} is probably cyclo-

Fig. 3.—Apparatus for the determination of proper density of high molecular weight fluorocarbons.

pentforane and the remainder of the C_5 material is probably a mixture of isomeric acyclic isomers. The properties of the six-carbon fraction indicate the presence of at least three individual compounds. Two cyclic compounds and a mixture of acyclic isomers were separated. One

cyclic compound is identified as cyclohexforane by its high melting point and comparison with a previously obtained compound (6). One relatively pure acyclic C_8F_{18} fraction was separated, but the rest of the eight-carbon fraction was unseparable, although continuously taken refractive index during distillation indicated at least five compounds. In the nine-carbon material there is at least one cyclic and one bi-cyclic compound. The bi-cyclic C_9F_{16} is presumably a compound with fused rings of five and six carbon atoms by comparison with a previously reported compound (7). The mono-cyclic compound is most likely a six-membered ring with three methforyl groups, as it has the properties of this compound as given previously (7). An individual compound was separated from higher-boiling material. It was a solid with liquid fractions boiling both immediately higher and lower. Its determined molecular weight of 580 corresponds to $C_{13}F_{22}$ and indicates the compound to consist of three fused six-membered rings arranged analogous to the hydrocarbon benzonaphthene. Material with boiling points above 240°C was solid at room temperature. The properties of compounds and fractions boiling above room temperature are given in Table III. Standard means of determining properties were used except for molecular weights above 400. For this a new density balance was designed (25), a diagram of which is shown in Fig. 3.

The Electrochemical Process (20)

INTRODUCTION

To produce fluorocarbons without the necessity of generating elementary fluorine has been a major objective from the time it was demonstrated that fluorocarbons containing more than three carbon atoms per molecule were stable and interesting substances. Although both the AgF_2 and the CoF_3 processes are examples of excellent technology and are capable of producing many desirable products, they require large amounts of equipment operated under very careful control and are, therefore, quite expensive. A number of chemically very skillful procedures have been devised to reduce greatly the amount of elementary fluorine required in the production of the finished fluorocarbon. In general, these procedures involve the replacement of hydrogen atoms on hydrocarbons by direct chlorination, then replacement of as much of the chlorine with fluorine as can be readily accomplished with the Swarts reaction or the halogen exchange with hydrogen fluoride, then perhaps a coupling or chlorine removal step, and finally replacement of the residual chlorine and hydrogen with elementary fluorine. This last step sometimes was the saturation of double bonds with the element, and for this

last step reagents such as AgF_2, CoF_3, and BrF_3, which required the element for their preparation, were sometimes used instead of the element itself. All these methods of preparation require the generation of as much elementary halogen as the direct fluorination with the element. The only advantage, which may not be an advantage in many cases, is the use of chlorine instead of fluorine for part of the necessary elementary halogen.

The electrochemical process produces fluorocarbons directly in one step without the employment or the generation of any elementary fluorine. It does this by replacement of hydrogen with fluorine on organic chemical substances dissolved in liquid hydrogen fluoride or in contact with liquid hydrogen fluoride made conducting with some electrolyte. It operates at potentials considerably below that necessary to generate the element. Hydrogen is generated simultaneously with the fluorocarbon; but as there is no reaction between these two products under conditions of cell operation, there is no need of separating cell compartments. This makes possible very compact cell design.

Many organic substances, particularly those containing oxygen, nitrogen, or sulfur, are not only soluble in liquid hydrogen fluoride but the solutions are highly conducting. Passage of an electric current through these solutions with suitable electrodes and at suitably low potentials results in the production of fluorocarbons or fluorocarbon derivatives or both. Some organic compounds such as hydrocarbons are only very slightly soluble in hydrogen fluoride or do not form electrically conducting solutions. These materials can, however, be used in the process by the simple expedient of adding some material, either organic or inorganic, which will provide conductivity.

GENERAL TECHNIQUE AND PROCEDURE

The cells are constructed of any metal not readily attacked by hydrogen fluoride such as copper or iron. There is only one compartment so the cell body serves merely as a vessel for the solution and a support for the electrodes. It can be part of the cathode. The electrodes most conveniently are arranged as a compact pack with alternating cathodes and anodes. Cathodes can be of almost any conductor such as iron, copper, or nickel. Anodes are usually nickel, but other metals show promise. Both hydrogen and gaseous products escape through a gas exit line. Separation of fluorocarbons from the hydrogen is accomplished by standard procedures such as condensation stripping. Liquid products are denser than the electrolytic solution and are drained from the bottom of the cell. Voltages can range up to about 8 volts depending on condi-

tions, but most situations operate at between 5 and 6 volts. The current densities are usually in the order of 0.02 amp. per square centimeter.

It is important that cell potentials be kept below that necessary for the generation of fluorine. If the potential is raised so that the element is produced, extensive corrosion of the electrodes occurs, some fluorine escapes and can be detected in the exit gas, minor or even major explosions occur, and undesirable decomposition of the organic materials results. Fluorocarbons are not satisfactorily produced under these conditions.
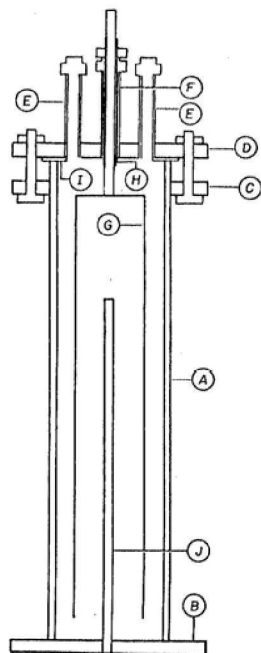
FIG. 4.—Electrochemical process laboratory cell.

The size or shape of the cell has little to do with the process. The first experiments used cells 1 in. in diameter and 6 in. high. At present a 2000-amp. cell is in operation. Intermediate sizes such as those carrying 5, 50, 100, and 200 amp. are also at present being employed. Any temperature of operation is satisfactory at which the electrolytic solution remains liquid. For laboratory purposes it has been convenient to hold the cells at or near 0°C so that an ice bath can be used. At this temperature loss of hydrogen fluoride by vaporization is not serious for laboratory operations. Higher temperatures can be used particularly if the cell is held under pressure. Various means can be used to return vaporized hydrogen fluoride to the cell such as low temperature stripping condensers on the gas exit line, with or without the aid of solvents.

A great variety of raw materials can be employed. Examples are: hydrocarbons, oxygen-containing organic compounds such as carboxylic acids, alcohols, ethers, and esters, nitrogen-containing compounds such as amines, and many other classes of substances. The products obtained include fluorocarbons, fluorocarbon hydrides, fluorocarbon chlorides, fluorocarbon oxides, fluorocarbon nitrides, fluorocarbon carboxylic acid fluorides, etc.

Some degradation of the carbon structure of the organic raw material occurs with some substances and under some conditions of operation. Carbon dioxide is produced in some cases from oxygen-containing materials as well as OF_2 and sometimes even CO. From nitrogen-containing substances NF_3 is sometimes a product. There is also some splitting of the carbon structure to form products containing fewer carbon atoms than the raw material, although usually the greatest amount of product

contains the same number of carbon atoms. A variety of products is obtained from the same source material. For example, a carboxylic acid R—CO₂H can give the fluorocarbon ⊖F containing the same number of carbon atoms as contained in R, with small amounts of smaller fluorocarbon molecules, fluorocarbon hydrides such as ⊖H, and also the acid fluoride ⊖COF. Resinous materials are produced in the cells in some cases but not in others. These resinous materials usually contain fluorine sometimes up to 50 or 60%.

CELL DESIGNS

A small fluorocarbon cell for laboratory use is shown in Fig. 4. The cell body is a piece of 3-in. iron pipe. The cell body and a central post
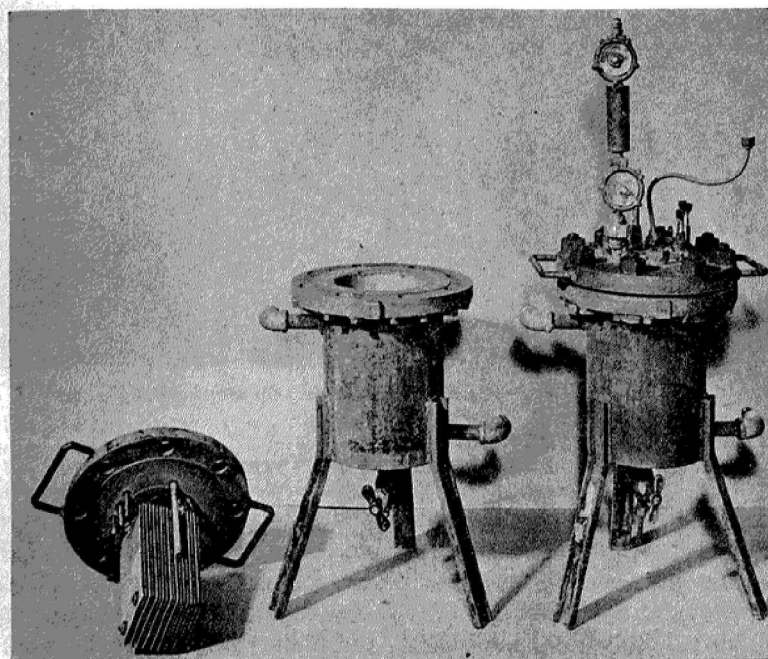

FIG. 5.—Electrochemical process—50 amp. cell.

serve as the cathode. The anode is a cylindrical piece of nickel sheeting with a longitudinal slit to provide circulation of liquid for the region inside the anode. In Fig. 5 is shown a photograph of a 50-amp. cell and in Fig. 6 a 2000-amp. cell. The fact that separation of anode and cathode compartments is not necessary, combined with the fact that there is small electrode corrosion, makes it possible to construct and use very compact

electrode arrangements. A high volume efficiency is thus provided. A cubic foot of volume of an electrode, consisting of interleaving metal plates making up the anode and cathode, can produce in a twenty-four-hour day between 5 and 50 lb. of product.
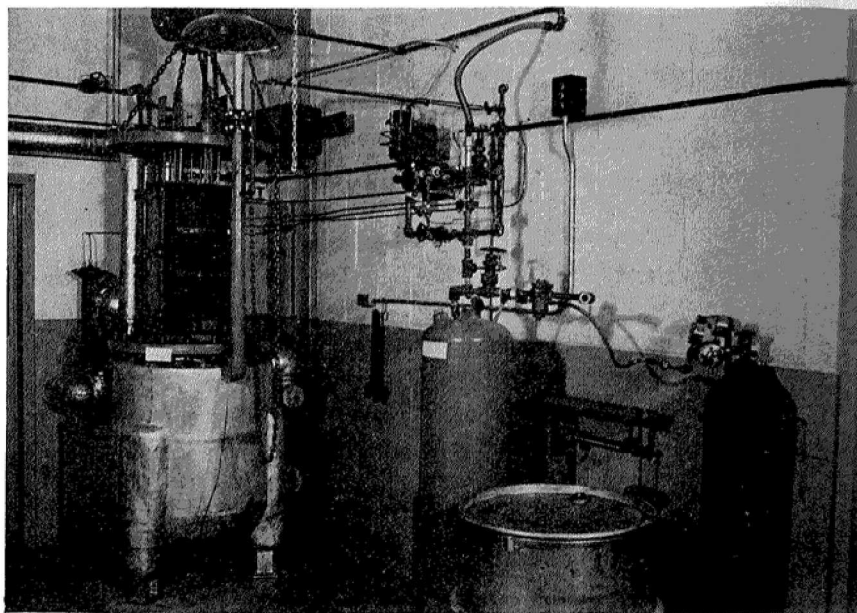

FIG. 6.—Electrochemical process—2000 amp. cell.

TYPICAL OPERATION OF PROCESS

In a typical laboratory operation using acetic acid, 11 kg. of methforane and 8 of fluoroform were produced. A current density of 0.04 amp. per square centimeter was used at voltages between 6.0 and 7.5. The exit gas analyzed for H_2 67%, CO_2 16%, OF_2 2.3%, CF_4 7.7%, CF_3H 5.6%, CF_2H_2 1.3%, and CFH_3 and higher-boiling products 0.3%.

Propionic acid gave 10 kg. of ethforane in a preparation which used a current density of 0.04 amp. per square centimeter at voltages between 5.5 and 7.0. The gas stream analyzed H_2 79%, CO_2 11%, OF_2 2.6%, CF_4 0.9%, C_2F_6 5.4%, C_2F_5H 0.9%, and $C_2F_4H_2$ 0.1%.

Other oxygen and nitrogen-containing organic compounds function in a manner not greatly different. The employment of a hydrocarbon or other relatively nonsoluble substance in the process is an unexpected variation of the technique. A typical operation using octane produced

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octforane as the major product. The original cell charge was 160 g. n-octane, 550 g. HF, and 10 g. H_2O. Water and hydrogen fluoride were added periodically as the experiment progressed, the hydrogen fluoride to maintain the liquid level and the water to provide conductivity. The total of these additions amounted to 440 g. of hydrogen fluoride and 60 g. of water for the passage of 47.3 faradays. There was produced 560 liters of gas not condensed at $-70°C$. From this 54 g. of CF_4, methforane, and 27 g. of C_2F_6, ethforane, were condensed in liquid air. In Dry-Ice traps 120 g. of product was collected during the experiment, and 14 g. by passing dry air through the cell at its conclusion. The distribution of products is shown in Table IV. Other substances besides water used to pro-

TABLE IV

Typical Distribution of Products from Octane Using Electrochemical Process

Boiling range, °C	Wt., g.	Mol. wt.	%F
−70 to 0	9		
0 to +30	7		
30 to 37	14.5	221–292	
37 to 52	3	285–303	
52 to 55	6.5	303–331	
55 to 70	6.5	330–335	79.1, 77.4
70 to 75	3.0	341	
75 to 85	4.0	381	
85 to 90	3.0	374	
90 to 95	11.0 ⎫		
95 to 96	52.5 ⎬	440–444	78.6
higher boiling	5.5 ⎭	(b.p. 102–103)	
losses	6.5		

vide conductivity in the production of octforane from octane were methanol, acetic acid, pyridine, sodium fluoride, ammonia, and mercuric cyanide.

Carboxylic acids $R—CO_2H$ or their anhydrides give in general the fluorocarbon containing the same number of carbon atoms per molecule as the hydrocarbon radical R, the same fluorocarbon with one hydrogen atom ⊝H fluorocarbons of few carbon atoms per molecule, some di and tri hydrogen compounds, carbon dioxide, some oxygen difluoride, and the compound ⊝COF where ⊝ is the fluorocarbon radical corresponding to R. Alcohols ROH give a range of fluorocarbons with the largest quantity appearing in the fraction in which the molecule has the same number of carbon atoms as R, some distribution of lower molecular weight fluorocarbons and a smaller amount in larger molecular weight compounds and some hydrogen-containing compounds. Ethers ROR′

give chiefly the fluorocarbon oxide ⊖ O ⊖ but also the fluorocarbon ⊖l
and ⊖′F. Similarly, the tertiary amines RR′R″N give the fluorocarbon
nitrides ⊖ ⊖′⊖″N as well as the fluorocarbons ⊖F, ⊖′F, ⊖″F. Primar
amines RNH₂ give chiefly the fluorocarbon ⊖F and NF₃.

Liquid Phase Fluorination

Elementary fluorine has been successfully caused to react with organi
compounds by means of several techniques, and replacement of hydroger
by fluorine has been accomplished by means of higher valence typ
metallic fluorides such as AgF_2 and CoF_3. There are, however, very fev
examples of a liquid phase fluorination reaction. The use of AgF_2 and
CoF_3 even with liquid reactants is a solid-liquid surface reaction. Mos
of the successful fluorinations with either elementary fluorine or witl
the metallic fluorides are accomplished with gaseous reactants. Some
reactions have been conducted with gaseous fluorine admitted to an
organic compound dissolved in a liquid solvent. Hydrogen fluoride has
been used for this purpose, and an example of its use is the fluorination
of acetophenone to difluoroacetophenone (24). This solvent, although
inert to the action of elementary fluorine, is an extremely acidic solvent
and for reactions in which acidity is disadvantageous, it cannot be used
Fluorine is also very slightly soluble in it, so that it is difficult to carry
out truly liquid phase reactions unless the organic reactant is in extremely
dilute solution and the fluorine is admitted very slowly. Otherwise the
reaction will take place at the gas-liquid boundary. Liquid fluorocarbons
are also available; but as hydrogen fluoride is produced by all reactions
in which hydrogen is replaced by fluorine, a solution of an organic sub-
stance in liquid fluorocarbon becomes acidic when fluorine reacts with
the organic substance. Although fluorine is more soluble in liquid fluoro-
carbon than in hydrogen fluoride, the solubility is still low and truly
liquid phase reactions will be exceptional. Chlorine-containing solvents
such as carbon tetrachloride or difluorodichloromethane give simul-
taneous chlorination and fluorination due to reactions of the solvent (1).
In addition the solubility of fluorine is low in these fluorine-containing
solvents, and the reaction takes place at the liquid-gas interface as
Bigelow has pointed out.

Liquid phase reactions have considerable advantages of economy,
specificity, and simplicity of operation and control; and it is highly
desirable to find conditions for liquid phase fluorination. The solvent
must be resistant to the action of elementary fluorine but should have a
high solubility for it, it should be a good solvent for organic substances,
and it should either be basic or should have a capacity for absorbing
hydrogen fluoride without becoming acidic. It has been found that at

low temperatures pyridine possesses all these desired qualities and at higher temperatures 2-fluoropyridine does likewise (23). Fluorine has a very considerable solubility up to about one mole of fluorine to one mole of solvent apparently to form the pyridine-perfluorides. The compounds are resistant to the action of the element, and organic compounds are soluble in it. In addition they absorb very large amounts of hydrogen fluoride without becoming acidic.

Fluorine was found to absorb smoothly and completely in liquid pyridine with apparent reaction but with no evidence of the production of gaseous products. The reaction mixture became dark in color and viscous as the reaction proceeded. Final separation of the reaction mixture showed that in addition to pyridine a considerable amount of 2-fluoropyridine had been formed. There was also a residue of 2-amino-pyridine. When the temperature of the pyridine during the admission of fluorine was held at $-40°C$, there was no evidence of apparent reaction and a dark brown solid separated from the liquid. This solid is apparently a molecular complex between fluorine and pyridine such as pyridine perfluoride $C_5H_5N \cdot F_2$. The solid disappeared as the temperature was allowed to rise to $0°C$, and there was a considerable evolution of heat. The product of the reaction, i.e., between pyridine and pyridine per-fluoride, was found to be 2-fluoropyridine.

As 2-fluoropyridine is more resistant to elementary fluorine than pyridine, it can be used as a liquid phase solvent for the element at temperatures at which fluorine reacts with pyridine. In the temperature range of $-10°C$ to room temperature 2-fluoropyridine absorbed fluorine completely in amounts of one mole of fluorine to one of 2-fluoropyridine with no apparent reaction. This mixture showed no evidence of reaction when heated until a temperature of $150°C$ was reached. The product of this reaction was found to be difluoropyridine. At room temperature fluorine is absorbed by 2-fluoropyridine with no apparent reaction. The solution remained clear, but as the quantity of dissolved fluorine increased it became viscous. When saturation was approached, the solution was a clear yellow-brown viscous liquid which became a glass at about $-30°C$. Its total fluorine content was found to be 47%, and it apparently consisted chiefly of 2-fluoropyridine perfluoride. It reacted vigorously with pyridine, acetophenone, and acetic acid. It liberated iodine from potassium iodide and reacted with sodium hydroxide.

The use of 2-fluoropyridine or similar nitrogen-containing organic compounds for liquid phase fluorination reactions provides an excellent means of controlling the reactions of elementary fluorine. It will be of considerable assistance in the production of fluorocarbons. It will be used in at least two different ways. In the one, it will be used as a

solvent for a liquid phase reaction between fluorine and an organic com pound. In the other, it will serve to dissolve a quantity of fluorin The resulting solution will then be used to mix with an organic compoun under controlled conditions for fluorination reactions.

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CHAPTER 13

Fluorocarbons—Their Properties and Wartime Development

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CONTENTS

Introduction

Prior to 1937 the only definitely known fluorocarbons were CF_4 and C_2F_6; in that year and more extensively in 1939 the preparation and properties of liquid fluorocarbons were disclosed by Simons and Block (86). Since then a tremendous expansion in the field of fluorocarbons has occurred due to a considerable extent to work on problems concerned with the separation of uranium isotopes. In July, 1940, the possibility of using fluorocarbons as sealants and coolants and in other applications in direct contact with uranium hexafluoride was suggested by J. H. Simons; all materials which had been tested previously were found to be unsuitable since they reacted with the corrosive uranium hexafluoride. In December of that same year a 2-cc. sample of liquid fluorocarbon, virtually all of the material available, was sent by Simons to Dr. H. C. Urey at Columbia University. Tests made on this small amount of material showed that it had the desired properties (28), and the problem then became one of finding suitable methods of preparing fluorocarbons on a large scale. Because of the secrecy surrounding all phases of atomic energy research at that time, fluorocarbons acquired the code name "Joe's Stuff"; this code name was derived, of course, from the given name of the person creating and supplying the first liquid fluorocarbon samples, J. H. Simons.

Out of the intensive search for suitable methods of preparing fluorocarbons which ensued several processes were developed. The two methods which were extensively investigated for large-scale production

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