MASTER

**High Voltage Research (Breakdown
Strengths of Gaseous and Liquid
Insulators) and Environmental Effects
of Dielectric Gases**

**Semiannual Report
(October 1, 1978—March 31, 1979)**

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Health and Safety Research Division

Atomic, Molecular and High
Voltage Physics Group

HIGH VOLTAGE RESEARCH (BREAKDOWN STRENGTHS OF
GASEOUS AND LIQUID INSULATORS) AND ENVIRONMENTAL
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ABSTRACT

Some economic aspects of gas insulated cables are discussed, especially with respect to the future use of improved gaseous dielectrics to reduce energy losses.

Electron attachment rates were measured for several haloethanes, and the attachment cross sections were obtained from them. Relations are being assessed between the attachment cross sections (especially when integrated over energy) and observed breakdown voltages. Attachment rates for perfluoro-n-alkanes are also being measured. The electron energy distribution functions for N_2 have been re-checked in view of their significance in the calculation of electron attachment cross sections from measured attachment rates.

The possibility of electron detachment from negative ions by either electric field, or by photons, or by electron impact, has been studied. The possible role of electron detachment in breakdown is being studied. Field induced detachment is shown to have no significant effect on breakdown.

The breakdown strength measurements on unitary gases continued; tests have been made on $1,1,1-C_2Cl_3F_3$ (1,1,1-trichlorotrifluoroethane), $1,1,2-C_2Cl_3F_3$ (1,1,2-trichlorotrifluoroethane or Freon 113), OCS (carbonyl sulfide), C_2ClF_5 (chloropentafluoroethane or Freon 115), and $1-C_3F_6$ (hexafluoropropene).

In the experimental study of breakdown strengths of mixtures, improvement was sought with two approaches: (1) seek better "moderator" gases for the promising attaching gases, and (2) seek effective *combi-*

nations of attaching gases. Breakdown tests were made on the systems CF_4/SF_6 and $\text{CF}_4/\text{c-C}_4\text{F}_8$ with moderator CF_4 (tetrafluoromethane). Tests were made of moderators CHF_3 (trifluoromethane), CH_2F_2 (difluoromethane), and 1,1,1- CH_3CF_3 (1,1,1-trifluoroethane) with SF_6 , $\text{c-C}_4\text{F}_8$ (octafluorocyclobutane), and 2- C_4F_6 (perfluoro-2-butyne). Other systems tested included $\text{SF}_6/\text{C}_2\text{ClF}_5$, $\text{c-C}_4\text{F}_8/\text{SF}_6$, 1- $\text{C}_3\text{F}_6/\text{SF}_6$, $\text{c-C}_4\text{F}_8/1-\text{C}_3\text{F}_6$, $\text{c-C}_4\text{F}_8/1,1,1-\text{CH}_3\text{CF}_3$, and OCS/SF_6 . For the first time we obtained significant synergism between a moderator and attaching gases other than SF_6 , a vital step to optimizing mixtures better than SF_6 .

In environmental studies, several projects proceeded well. The electron impact fragmentation of 1,1,1- $\text{C}_2\text{Cl}_3\text{F}_3$ was studied. Several stress cells were used to begin testing SF_6 and $\text{c-C}_4\text{F}_8$ for long-term decomposition. A detailed analysis of 2- C_4F_6 and SF_6 breakdown products was made. The new high pressure quadrupole mass spectrometer gave preliminary results on breakdown products of SF_6 , dry air, and CF_4 . A critical literature review of SF_6 breakdown products was completed.

In the impulse apparatus, many binary and ternary mixtures of $\text{c-C}_4\text{F}_8$, SF_6 , and N_2 were tested with lightning surge in point-plane geometry. Certain advantageous mixtures were found.

In the applied studies apparatus testing was done on two candidates as moderator gases (CF_4 and 1,1,1- $\text{C}_2\text{F}_3\text{H}_3$) with several promising attaching gases. Cylindrical electrode geometry with both smooth and rough surfaces was used, and under these "practical" conditions significant synergism was again obtained between a moderator and an attaching gas superior to SF_6 . A new high pressure chamber and power supply were installed in this apparatus. Triggered gap, or "diverter" studies were resumed.

The liquid breakdown experiment was satisfactorily de-bugged with the study of the effect of various particle filters on breakdown voltage, and observed breakdown voltages of liquid n-hexane were in agreement with measurements by others.

Planning for the Second Symposium on Gaseous Dielectrics proceeded well. In February about 500 advance programs, prepared with the advice of the International Committee, were mailed.

I. INTRODUCTION

This report covers our progress on High Voltage Research (breakdown strengths of gaseous and liquid dielectrics) and also our progress on the environmental effects of gaseous dielectrics.

Gas-insulated gear using SF_6 has gained wide acceptance in this decade. As an introduction to this progress report, we outline certain aspects of energy transmission and distribution that suggest the future cost of energy is greatly increasing the need for gas-insulated apparatus. This cost of energy has in the past been deemed small relative to the cost of materials, but in the near future the cost of losses will play an ever increasing role compared with the cost of materials. In the following we find that *present* SF_6 transmission systems are favored *economically* even by analyses that still use *modest* cost estimates of future energy. We also find that improved new gaseous dielectrics can reduce loss costs much further compared to SF_6 insulated systems. For example, some of the gaseous dielectric mixtures already under test in this program are providing sufficient improvement over SF_6 to deliver substantial savings in energy.

The nation faces one of the greatest challenges of its life in balancing its energy consumption and production. At stake are national security, economic vitality, and the value of the dollar. Therefore, we have to consider the need to conserve, *in the transmission stage*, electricity--our fastest growing form of energy.¹ In addition to economic, other advantages of enclosed transmission are obvious; environmental objections (due to fields, land use, aesthetics, etc.) insulator contamination, lightning problems, and right-of-way requirements are all reduced.

A detailed economic comparison of the major methods of underground electric power transmission has recently been completed for the Department of Energy (DOE) by the Philadelphia Electric Company, with input from 16 utilities, manufacturers, and laboratories.² Several underground systems were studied for carrying 10,000 MW from a hypothetical energy park to Philadelphia along an existing aerial right-of-way including rural, suburban, and urban areas. The costs were calculated to include compensation, capitalized energy and maintenance losses, and right-of-way, for a 40-year lifetime if installed in 1995. By this "present worth" calculation, the SF₆-insulated systems were among the most economical; the only alternatives projected more economical in 1995 than the 500 kV 3-phase SF₆ rigid system were aerial and 230 kV superconducting cable.

Transmission losses were also studied in the Philadelphia Electric Company report.² In the present worth calculations, they were charged at a modest 5% inflation rate and at 9 1/4% annual interest rate. No value was attached to the national economic and security interests in conservation and energy independence. Therefore, let us examine the losses separately.

It is seen from Table 1 that the gas insulated transmission line (GITL) systems also compare well in terms of losses, and in fact the rigid forms are the most energy efficient AC systems currently in use. (No DC gas-insulated system was studied.)

In the future, improved gaseous dielectrics will allow us to lower the cost of the GITL systems (e.g., see p. 321 of ref. 2). A thorough *economic* review of the effect of improved gaseous dielectrics will

Table 1. Losses from the Philadelphia Electric Company report

System	Losses (Gigawatt-hours per year)
HPOPT, 500 kV cellulose	1,092
HPOPT, 500 kV PPP	733
HPOPT, 765 kV PPP	539
forced cooled, 500 kV PPP	2,144
forced cooled, 765 kV PPP	1,666
SCOF, 500 kV AC	469
SCOF, 600 kV DC	213
SF ₆ GITL - 3 ϕ rigid	326
SF ₆ GITL - 1 ϕ rigid	389
SF ₆ GITL - 1 ϕ flexible	671
SC, 230 kV AC	611
SC, rigid, 230 kV AC	1,111
SC, 300 kV DC	120
Aerial/underground	470
Resistive cryogenic	3,550

(Acronyms: HPOPT = high pressure oil filled pipe-type; PPP = paper, polypropylene; SCOF = self-contained oil filled; GITL = gas-insulated transmission line; SC = superconducting; aerial/overhead = system with 60 miles aerial and 6 miles of 3 ϕ GITL.)

not be undertaken here at this time, but we can see the *energy conservation* potential of improved dielectrics. Consider, for example, the 345 kV (362 kV AC max) Westinghouse GITL currently in use.^{3,4} In present 3-phase systems, the sheaths generally carry negligible current and the three inner aluminum alloy conductors (resistivity $\approx 4 \times 10^{-6}$ ohm - cm) carry the load current. The AC resistance of such a conductor with a given outer diameter is *minimized by choosing a hollow core of appropriate diameter*, which can be found from refs. 5, 6, and 7. In Table 2, losses for this 3-phase cable are given. The current, voltage, and sheath size are the same for each case. Improvement in the gaseous dielectric is exploited to allow the conductor to be enlarged to the diameter where the peak AC field at its surface is that at which the gaseous dielectric is rated. After the outer conductor diameter is selected, its hollow core diameter is chosen to minimize the AC resistance at 60 Hz, thus reducing loss via dielectric improvement.

Table 2. Reduced losses for improved gaseous dielectrics

Rated gaseous dielectric E-field (kV/in.)	System loss ($\frac{\text{kW}}{\text{mile}}$)(3 ϕ)
109 ^a	180 ^b
109	154 ^{c, d}
200	66.6 ^{c, d}
300	60.3 ^{c, d}
500	55.8 ^{c, d}

^aApproximate peak E-field in present 345 kV SF₆-insulated cable, ref. 4.

^bCalculated from dimensions in ref. 3; not optimized for minimum AC resistance.

^cCalculated using minimum AC resistance for conductor diameter giving rated dielectric E-field.

^dIn each case the hollow core size is chosen to minimize AC resistance.

The system loss can be greatly reduced with improvement in insulation strength (Table 2). Since the sheath size in this example is constant (14-in. diameter) the effect of higher E field on loss "saturates" as the conductor size approaches sheath size, and then by increasing the sheath size one could continue to lower the losses as the gas dielectric is improved. Of course, the conductor that is optimum for minimum loss has more capital cost than one with less material. If energy rates continue to escalate rapidly (more than the 5% rate considered in ref. 2), and if the economic and political values of energy independence are considered very high, then we should place very high value on improved gaseous dielectrics for GITL and associated gear.

Many gaseous dielectric mixtures already under test in this program have demonstrated performances at 1 atmosphere that suggest that at the higher compressed gas insulated (CGI) cable pressures they can insulate fields on the order of those in Table 2. Testing at these higher pressures is presently underway, and still better mixtures are being developed. The above example is intended to show only one way that improvement in gaseous dielectrics can be used to improve a GITL.

II. BASIC STUDIES OF GASEOUS DIELECTRICS

A. Electron Attachment

(i) Electron Attachment to Haloethanes

In collaboration with Professor D. L. McCorkle of the Physics Department of the University of Tennessee, Knoxville, measurements have been made of the electron attachment rates as functions of the mean electron energy $\langle \epsilon \rangle$ and determination of the electron attachment cross sections as functions of the electron energy ϵ using the electron swarm method for a number of haloethanes for which breakdown strength data exist or are in progress at our laboratory. Figure 1 shows the electron attachment rates as functions of $\langle \epsilon \rangle$ for 1,1,1- $\text{C}_2\text{F}_3\text{Cl}_3$, 1,1,2- $\text{C}_2\text{F}_3\text{Cl}_3$, 1,1,1- $\text{C}_2\text{Cl}_3\text{H}_3$, and 1,1,2- $\text{C}_2\text{Cl}_3\text{H}_3$. The data on 1,1,1- $\text{C}_2\text{Cl}_3\text{H}_3$ and 1,1,2- $\text{C}_2\text{Cl}_3\text{H}_3$ are from our earlier studies.⁸⁻¹⁰ The effect of F substitution, as well as the effect of the number and relative positions of the Cl atoms in the molecule, is evident. Attention should be drawn to the large electron attachment rates for 1,1,1- $\text{C}_2\text{F}_3\text{Cl}_3$. These results and those on 1,1- $\text{C}_2\text{F}_4\text{Cl}_2$ and 1,2- $\text{C}_2\text{F}_4\text{Cl}_2$ in Fig. 2 are being analyzed and prepared for open literature publication.

From the data in Figs. 1 and 2 (upper portion) the attachment cross sections $\sigma_a(\epsilon)$ have been determined and are shown in Figs. 2 (lower portion) and 3. From these figures and Table 3, it is evident that

- (1) replacement of H by F lowers the positions of the resonance maxima and increases the magnitude of $\sigma_a(\epsilon)$;

Fig. 1. Electron attachment rate, αw , versus mean electron energy, $\langle \epsilon \rangle$ for 1,1,1- $\text{C}_2\text{F}_3\text{Cl}_3$ (1,1,1-trichlorotrifluoroethane), 1,1,2- $\text{C}_2\text{F}_3\text{Cl}_3$ (1,1,2-trichlorotrifluoroethane), 1,1,1- $\text{C}_2\text{Cl}_3\text{H}_3$ (1,1,1-trichloroethane), and 1,1,2- $\text{C}_2\text{Cl}_3\text{H}_3$ (1,1,2-trichloroethane).

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Fig. 2. Electron attachment rate versus mean electron energy (upper portion) and total electron attachment cross section as a function of electron energy (lower portion) for 1,1- $\text{C}_2\text{F}_4\text{Cl}_2$ [1,1-dichlorotetrafluoroethane (Freon 114)] and 1,2- $\text{C}_2\text{F}_4\text{Cl}_2$ (1,2-dichlorotetrafluoroethane).

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Fig. 3. Electron attachment cross section versus electron energy for 1,1,1- and 1,1,2- $\text{C}_2\text{F}_3\text{Cl}_3$ and 1,1,1- and 1,1,2- $\text{C}_2\text{Cl}_3\text{F}_3$.

Table 3. Electron attachment cross section maxima, values of $\sigma_a(\epsilon)$ at these maxima, energy integrated cross sections, thermal attachment rates, and DC uniform field breakdown voltages for haloethanes

Haloethane compound	ϵ_1 (eV)	ϵ_2 (eV)	ϵ_3 (eV)	$\sigma_a(\epsilon_2)$ (10^{-16} cm 2)	$\sigma_a(\epsilon_3)$ (10^{-16} cm 2)	$\int_{0.04 \text{ eV}}^{1.4 \text{ eV}} \sigma_a(\epsilon) d\epsilon$ (10^{-16} eV cm 2)	$(V_S)_R^a$	Thermal attachment rate (sec $^{-1}$ torr $^{-1}$)
1,1,1-C $_2$ F $_3$ Cl $_3$	<0.05	0.16	0.65	64	14.6	13.5	~2.5	8.93×10^9
1,1,1-C $_2$ H $_3$ Cl $_3$	<0.05	0.10	0.79	3.6	3.1	1.74		4.72×10^8
1,1,2-C $_2$ F $_3$ Cl $_3$	<0.05	0.25	0.73	10	8.1	5.94		3.59×10^8
1,1,2-C $_2$ H $_3$ Cl $_3$	0.05	0.33	0.85	1.1	2	1.02		5.8×10^6
1,1-C $_2$ F $_4$ Cl $_2$	<0.05	0.25	0.80	3.0	3.8	3.22		1.57×10^8
1,2-C $_2$ F $_4$ Cl $_2$	~0.05	0.33	0.95	2.1	2.1	1.85		2.28×10^7

^aUniform field DC breakdown strength relative to SF $_6$ of one (see Fig. 4).

- (2) the 1,1,1- or 1,1- isomers capture electrons much more efficiently than the 1,1,2- or 1,2- isomers; the positions of the resonance maxima are lower for the former than for the latter; and the dipole moments of the 1,1,1- or 1,1- compounds are as a rule greater than those of the 1,1,2- or 1,2- isomers; and
- (3) the magnitude of $\sigma_a(\epsilon)$ increases with increasing numbers of Cl atoms in the molecule.

Although the attachment cross sections reported here are *total* (i.e., for all negative ions produced), our earlier work on similar compounds¹⁰ indicated that the predominant ion is Cl^- . Other ions [e.g., Cl_2^- or (parent molecule less one chlorine atom)⁻] are produced but with much lower yields. The present results, as well as our earlier studies on aliphatic halocarbons,¹⁰ show that the cross sections for electron attachment to these compounds are large and that the electron attachment process proceeds through a multiplicity of negative ion states.

Although a detailed comparison of these data with the respective breakdown strengths will have to await completion of the breakdown strength measurements currently in progress at our laboratory, we wish to report in this section our findings on 1,1,1- $\text{C}_2\text{Cl}_3\text{F}_3$. In Fig. 4, the DC uniform field V_S vs Pd data are plotted for 1,1,1- $\text{C}_2\text{Cl}_3\text{F}_3$ and SF_6 . The breakdown data for the two gases were taken under identical conditions. It is seen that the uniform field DC dielectric strength of 1,1,1- $\text{C}_2\text{Cl}_3\text{F}_3$ is ~ 2.5 times higher than that of SF_6 . This compares nicely with the $\sigma_a(\epsilon)$ data for the two gases shown in Fig. 5. It is seen that the

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Fig. 4. V_s versus Pd for 1,1,1- $\text{C}_2\text{Cl}_3\text{F}_3$ and SF_6 (see text).

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Fig. 5. Comparison of $\sigma_a(\epsilon)$ for 1,1,1-C₂Cl₃F₃ and SF₆. The data on $\sigma_a(\epsilon)$ for 1,1,1-C₂Cl₃F₃ are from Fig. 3; those on SF₆ are the swarm-unfolded cross sections for SF₆ using the new set of electron energy distribution functions for N₂ [see Sect. II A (iii)].

$\sigma_a(\epsilon)$ for 1,1,1- $\text{C}_2\text{Cl}_3\text{F}_3$ is not only larger than for SF_6 , but it is also shifted to higher energies. This allows for a better overlap between $\sigma_a(\epsilon)$ and the electron energy distribution functions for the case of 1,1,1- $\text{C}_2\text{Cl}_3\text{F}_3$, and as we explained earlier (see for example refs. 11 and 12), results in a higher V_s .

(ii) Attachment of electrons to perfluoro-n-hexane*

We have measured the electron attachment rate of perfluoro-n-hexane ($\text{n-C}_6\text{F}_{14}$) using N_2 as the buffer gas. The partial pressure of $\text{n-C}_6\text{F}_{14}$ ranged from 1 to 20 μ . The pressure of the nitrogen ranged from 500 to 4000 torr. A typical example of the dependence of the electron attachment rate for $\text{n-C}_6\text{F}_{14}$ on $\langle\epsilon\rangle$ is shown in Fig. 6. Note the *increase* in the attachment rate with increasing $\langle\epsilon\rangle$, which indicates that the maximum of the attachment rate for the electron capturing process is at a mean electron energy >0.8 eV.

There is also a slight increase in the attachment rate with increasing N_2 pressure. This increase indicates that not all of the $\text{n-C}_6\text{F}_{14}^{-*}$ ions are stabilized at the N_2 pressures that we have used, due possibly to the formation of very short-lived negative ions. Both the increase in the electron attachment rates with increasing mean electron energy above thermal and the existence of very short-lived negative ions are manifestations of trends in the electron attachment properties of the perfluorinated n-alkanes. As the size of the perfluoro-n-alkanes increases, the electron affinity of the parent molecule increases, and so do the lifetimes of the parent negative ions and their respective attachment cross sections (see a discussion in refs. 11 and 12). The

*These measurements were taken by S. Ghemati, a graduate student from the University of Tennessee.

Fig. 6. Electron attachment rate versus mean electron energy for n-C₆F₁₄ (perfluoro-n-hexane). (N₂ pressures: 500 and 2000 torr; n-C₆F₁₄ pressure: 20 μ .)

systematic study of the electron attachment properties of the perfluoro-n-alkanes will explain the influence of molecular size and molecular structure on the electron attachment properties of polyatomic dielectrics.

(iii) SF_6 revisited

In our determinations of the electron attachment cross sections, $\sigma_a(\epsilon)$, as functions of electron energy from the measured electron attachment rates, $\alpha w(\langle \epsilon \rangle)$, as functions of mean electron energy $\langle \epsilon \rangle$ --via the swarm unfolding technique¹³--we have been using a set of electron energy distribution functions, $f_{\text{N}_2}(\epsilon, E/P)$, for N_2 that were based on electron scattering cross sections $\sigma_{\text{sc}}(\epsilon)$ obtained over one decade ago.¹⁴ Recently, new $\sigma_{\text{sc}}(\epsilon)$ data for N_2 have become available, and new $f_{\text{N}_2}(\epsilon, E/P)$ for N_2 have been determined¹⁵ using these $\sigma_{\text{sc}}(\epsilon)$ data. The new electron energy distribution functions for N_2 are in good agreement with the old ones and the unfolded $\sigma_a(\epsilon)$ using the old and the new f_{N_2} (e.g., for the fluoro-carbon dielectrics in Appendices A and B) are in excellent agreement (Fig. 7).¹⁵ At low energies, however, there are minor differences between the old and the new $f_{\text{N}_2}(\epsilon, E/P)$, which seem to affect the detailed shapes of the $\sigma_a(\epsilon)$ functions when a *weak* resonance peak is close to an *intense* one. In view of this, we considered it necessary to unfold $\sigma_a(\epsilon)$ for SF_6 using the attachment rates of Christophorou et al.¹⁶ and the new f_{N_2} , and to compare the resulting $\sigma_a(\epsilon)$ with that we reported earlier (Table 4).

The $\sigma_a(\epsilon)$ for SF_6 functions agree for $\epsilon \lesssim 0.1$ eV (in this energy range SF_6^- ions are predominantly formed), but they differ in the energy range around 0.3 eV where SF_5^- ions are produced. In Fig. 7 the sum of the cross sections for SF_6^- and SF_5^- reported by Kline et al.¹⁷

Fig. 7. Comparison of electron attachment cross sections for SF_6 .
 — swarm unfolded cross sections reported in our earlier reports and publications using our old f_{N_2} and the attachment rates for SF_6 of ref. 16.
 ---- as for — but using the new f_{N_2} (see text and ref. 17).
 ○ $\sigma_{\text{SF}_6^-} + \sigma_{\text{SF}_5^-}$ of ref. 17.
 -●- $\sigma_{\text{SF}_5^-}$ of ref. 16.

are also plotted (open circles), as well as the cross section for formation of SF_5^- reported in 1971 by Christophorou et al.¹⁶ (closed circles). It is seen that the data of Kline et al.¹⁷ are in excellent agreement with our work below ~ 0.1 eV, but they are somewhat low for $\epsilon \gtrsim 0.2$ eV.

The comparisons we have made in the past between $\sigma_a(\epsilon)$ and the breakdown strengths of SF_6 and perfluorocarbons are unaffected by the uncertainty in the $\sigma_a(\epsilon)$ for SF_6 around 0.3 eV. The new f_{N_2} will be adopted in our future work.

Table 4. Values of the energy integrated attachment cross sections for a number of gaseous dielectrics using the old and the new electron energy distribution functions for N_2

Dielectric gas	$\int_{0.04 \text{ eV}}^{1.4 \text{ eV}} \sigma_a(\epsilon) d\epsilon$ $(10^{-16} \text{ cm}^2 \text{ eV})$	
	Old f_{N_2}	New f_{N_2}
SF_6	11.7	11.2
c- C_4F_6	5.3	5.08
2- C_4F_6	13.1	12.9
1,3- C_4F_8	10.7	10.5
c- C_4F_8	9.8	9.7
2- C_4F_8	7.3	7.2
c- C_7F_{14}	26.1	26.6
1- C_7F_{14}	4.3	4.4

B. Electron Detachment

(i) Electric-Field Induced Detachment

As we have indicated in our last semiannual report,¹⁸ a host of observations in breakdown studies have been attributed to electric field-induced electron detachment from negative ions. Very little, however, is known about this process, and its implied role in breakdown phenomena. Some work has been reported earlier in connection with particle accelerators. For example, the field-induced detachment from the simple atomic negative ions He^- ($1s2s2p$), H^- ($1s^2$), and D^- ($1s$)² has been studied (refs. 19-21, 20-24, and 25, respectively). Constant uniform electric fields of the order of 100 kV/cm and 2MV/cm were found to be necessary to detach electrons from He^- and H^- , respectively. The binding energy of the electron in He^- ($1s2s2p$) and H^- ($1s^2$) is 0.075 and 0.75 eV, respectively.¹⁴

We have addressed ourselves to this question recently; and in our last semiannual report,¹⁰ we presented Schweinler's (Appendix C)¹⁸ preliminary result on the probability per second, p , for electric-field induced detachment from atomic and molecular anions in s-states (angular momentum quantum number $\ell = 0$). The probability p was expressed in terms of the electron affinity, EA, the "size" of the anion, and the electric field strength, E . On the basis of these calculations, we argued that most likely it is the effect of the electric field on the transient ion AX^{*-} rather than on the stable ions AX^- or X^- (final products of non-dissociative and dissociative electron attachment) that determines the probability of field-induced detachment, (i.e., the detachment of the loosely bound electron from the high-lying levels of AX^{*-} that is very sensitive to electric fields).

In this report we outline (see Appendix C) our preliminary results on the electric field-induced detachment from mononegative (atomic and molecular) anions, in states with angular momentum quantum numbers, ℓ , equal to 0, 1..., 4. These calculations show that as ℓ increases the value of p decreases for a fixed EA and E . In Table 5 the probability per second p is given for $\ell = 1$ and various combinations of EA and E . Similar data have been determined for $\ell = 2, 3$, and 4. The relevance of these calculations to gaseous dielectrics is being assessed. We might point out, however, at this stage that in many gas-discharge experiments where electron detachment was invoked to explain a rise in current at high values of E/P (e.g., in SF_6 at $E/P \gtrsim 100 \text{ V cm}^{-1} \text{ torr}^{-1}$; $T = 20^\circ\text{C}$; pressure = 5.2 torr) the electric fields were too low for any significant electric field-induced detachment. The reported increase in electron current in these studies, therefore, should be due to other processes. These can be either other electron detachment mechanisms (e.g., electron-impact induced detachment, photodetachment, associative and non-associative collision detachment, detachment in ion-excited molecule collision) and/or possible new processes that set-in at high E/P values and produce fragile (attached electrons weakly bound) primary or secondary new ions. We intend to look into these other electron detachment processes in the future.

Table 5. Values of p for $z = 1$ and various combinations of EA and E ; $x = 2^a$ and $f = 0.01^b$

EA(eV)	P(sec ⁻¹)								
	E(10 ⁶ volts cm ⁻¹)								
	0.01	0.1	0.5	1	2	5	10	20	50
0.01	1.41×10^6	6.6×10^9	5.71×10^{10}	1.22×10^{11}	2.53×10^{11}	6.45×10^{11}	1.3×10^{12}	2.61×10^{12}	6.53×10^{12}
0.03	5.35×10^{-7}	3.99×10^8	3.42×10^{10}	9.74×10^{10}	2.33×10^{11}	6.47×10^{11}	1.34×10^{12}	2.73×10^{12}	6.9×10^{12}
0.05		6.99×10^6	1.57×10^{10}	6.75×10^{10}	1.98×10^{11}	6.21×10^{11}	1.342×10^{12}	2.79×10^{12}	7.13×10^{12}
0.08		2.95×10^3	3.46×10^9	3.24×10^{10}	1.41×10^{11}	5.59×10^{11}	1.304×10^{12}	2.817×10^{12}	7.38×10^{12}
0.1		6.51	1.04×10^9	1.8×10^{10}	1.063×10^{11}	5.08×10^{11}	1.26×10^{12}	2.81×10^{12}	7.49×10^{12}
0.15		9.69×10^{-8}	2.97×10^7	3.14×10^9	4.57×10^{10}	3.75×10^{11}	1.12×10^{12}	2.72×10^{12}	7.67×10^{12}
0.3		3.42×10^{-39}	1.69×10^1	2.54×10^6	1.39×10^9	1.00×10^{11}	6.19×10^{11}	2.17×10^{12}	7.60×10^{12}
0.5			1.15×10^{-10}	7.08	2.48×10^3	8.7×10^9	1.95×10^{11}	1.30×10^{12}	6.72×10^{12}
1				6.06×10^{-19}	8.25×10^{-4}	1.64×10^6	3.03×10^9	1.84×10^{11}	3.58×10^{12}
1.5					3.85×10^{-16}	2.15×10^1	1.21×10^7	1.29×10^{10}	1.39×10^{12}
2.0						3.34×10^{-5}	1.54×10^4	5.15×10^8	4.24×10^{11}
3.0						3.98×10^{-13}	2.07×10^{-3}	2.11×10^5	2.22×10^{10}
5.0							5.77×10^{-21}	4.43×10^{-4}	9.86×10^6
8.0								8.03×10^{-21}	2.75

^a r_0/a_H where r_0 is roughly the negative ion radius and a_H is the Bohr radius.

^bFraction of probability density outside of the effective range, r_0 , of the interaction potential.

(ii) Photon-Induced Electron Detachment (Photodetachment)

An order of magnitude calculation* has shown that--for breakdown in an electron attaching gas where a substantial portion of the electrode gap contains negative ions--photodetachment may play a role in the dynamics of breakdown if the ion density is high (e.g., $\sim 10^9$ ions/cm³).

(iii) Electron-Impact-Induced Electron Detachment

There has been little work done on electron-impact-induced electron detachment from negative ions. A few measurements have been reported on the detachment of electrons from atomic anions (H⁻, C⁻, O⁻, F⁻). The cross section, σ_{ed} , for electron-impact-induced detachment is a function of the electron energy and the anion.¹⁴⁻²⁷ Values of σ_{ed} as high as 5×10^{-15} cm² have been reported.²⁷

*The number density of photodetached electrons per second, n_d , can be estimated from

$$n_d = n_i \int_{\nu > \nu_{th}}^{\infty} \sigma_{pd}(\nu) F(\nu) d\nu,$$

where n_i is the number density of negative ions, $\sigma_{pd}(\nu)$ is the photodetachment cross section for photons of frequency ν , $F(\nu)$ is the photon flux (photons sec⁻¹ cm⁻²) as a function of ν , and ν_{th} is the photodetachment threshold frequency. If we assume $n_i = 10^{10}$ ions cm⁻³, $\int_{\nu > \nu_{th}}^{\infty} F(\nu) d\nu = 10^{16}$ photons sec⁻¹ cm⁻² and that each of these photons has sufficient energy ($h\nu \geq h\nu_{th}$) to detach the electron from the negative ion with an average cross section of 10^{-17} cm², we find that n_d is $\sim 10^9$ sec⁻¹ cm⁻³.

Let us, then, take $\sigma_{pd} = 5 \times 10^{-15} \text{ cm}^2$, assume a (maximum) density of negative ions, n_i , of $10^{10} \text{ ions/cm}^3$, and determine the distance, $x_{2.72}$ at which the electron density would increase by a factor of $e (= 2.72)$ due *solely* to the electron detachment from negative ions via electron impact. We may write for the rate of increase of electron density with x

$$\frac{dn_e}{dx} = f \sigma_{ed} n_i n_e$$

or
$$\frac{dn_e}{n_e} = f \sigma_{ed} n_i dx$$

or
$$n_e = n_0 e^{f \sigma_{ed} n_i x},$$

where f is the fraction of electrons with energies high enough to induce detachment, and n_0 is the electron density at $x = 0$. If we take the most favorable case for which $f = 1$ we have

$$x_{2.72} = \frac{1}{\sigma_{ed} n_i} = 2 \times 10^4 \text{ cm},$$

which is clearly of negligible significance in discharges of laboratory size.

(iv) Ion-Neutral Induced Collisional Detachment

We shall elaborate on this process in our next report.

C. Dipole Scattering and Its Possible Effect on V_s

We have continued our investigation of gas dielectric components comprising molecules with permanent electric dipole moments, D , in pursuit of increased breakdown voltages, V_s , for multicomponent gaseous insulators.

The scattering cross section for thermal and epithermal electrons by polar molecules is known to be a very strong function of D .^{14,28} Actually, comprehensive work at our laboratory²⁸ has shown that for molecules with electric dipole moments in the range $0.6 \lesssim D \lesssim 4.1$ debye, the experimentally determined scattering cross sections for electrons having a maxwellian energy distribution ($T \approx 298^\circ\text{K}$) are, as a rule, within 50% of those calculated from the Born approximation theory of Altshuler.²⁹ Altshuler's calculation predicts that the momentum transfer cross section, $\sigma_m(v)$ is

$$\sigma_m(v) = \frac{1.72 D^2}{v^2} \quad (D \text{ in debye units}). \quad (1)$$

In analyses of swarm electron transport data at thermal and near thermal energies the electron scattering cross section, $\sigma_{sc}(v)$ was approximated by²⁸

$$\sigma_{sc}(v) = \frac{A_I}{v^2}, \quad (2)$$

where A_I is a constant and v is the electron velocity--and values of A_I were determined²⁸ for a large number of polar molecules with $D \lesssim 4$ debye.

The extent of electron energies above thermal over which expression (2) [or (1)] is valid is not known.¹⁸ To investigate this, we looked into the behavior of two polar molecules, namely, H_2O ($D = 1.85$ debye)

and NH_3 ($D = 1.46$ debye), which have been studied by the electron swarm method at thermal energies (unfortunately the beam work was restricted to $\epsilon \gtrsim 2$ eV). The swarm work²⁸ provided values for the constant A_I in Eq. (2) of $10.69 \text{ cm}^4 \text{ sec}^{-2}$ and $5.82 \text{ cm}^4 \text{ sec}^{-2}$ for H_2O and NH_3 , respectively. Using these values for A_I and assuming that Eq. (2) is valid up to ~ 6 eV, we determined for H_2O and NH_3 the scattering cross sections shown in Fig. 8. These are compared (see Fig. 8) with the total electron scattering cross sections obtained by the beam method³⁰ at higher energies. As can be seen, the cross sections predicted by Eq. (2) at energies $\gtrsim 2$ eV are not incompatible with the beam data for these molecules, although the higher values of the beam data for $\epsilon \gtrsim 4$ eV are obviously due to scattering processes other than electron-dipole scattering, which set in as ϵ increases. Thus, it could be assumed that for $\epsilon \lesssim 3$ eV the scattering cross sections determined from Eq. (2) are good estimates of the total electron scattering cross sections in this energy range. Furthermore, since the theoretical and the experimental scattering cross sections for dipolar molecules are not too dissimilar,^{14,28} Eq. (1) can be used to determine $\sigma_m(v)$ for polar molecules in the absence of experimental data. Thus, we calculated $\sigma_m(v)$ using Eq. (1) for $D = 2$ and 3 debye. These data are plotted in Fig. 9 and indicate that dipole scattering cross sections can indeed be very large for high D values ($\gtrsim 3$ debye) at low energies compared to other electron scattering processes. The role of dipole scattering in V_S for multicomponent gas dielectrics is being assessed, especially in combination with indirect electron scattering via negative ion resonances. Some of our findings on multicomponent gaseous dielectrics containing one dipolar component are presented in Sect. III B.

Fig. 8. Scattering cross sections as functions of electron energy

NH_3 : ---- based on the thermal electron scattering cross section data of Christophorou and Christodoulides²⁸ which suggested that $\sigma_{\text{sc}} = 5.82 \text{ V}^{-2} (\text{cm}^2)$.

● Total electron scattering cross section data of Brüche.³⁰

H_2O : — based on the thermal electron scattering cross section of Christophorou and Christodoulides²⁸ which suggests that $\sigma_{\text{sc}} = 10.69 \text{ V}^{-2} (\text{cm}^2)$.

○ total electron scattering cross section data of Brüche.³⁰

Fig. 9. Various cross sections as functions of ϵ .
 --- electron attachment cross section, $\text{SF}_6(\sigma_a)$, for SF_6 [see Sect. II A (iii)].
 --- electron attachment cross section, $2\text{-C}_4\text{F}_6(\sigma_a)$, for $2\text{-C}_4\text{F}_6$ (see Appendix A).
 — maximum s-wave capture cross section.
 $\text{N}(\sigma_T)$ and $\text{CO}(\sigma_T)$ are total electron scattering cross sections for N_2 and CO , respectively. σ_D and $\sigma_{D=3}$ are the electron-electric dipole scattering cross sections determined from Eq. (1) for D values equal to 2 and 3 debye respectively (see text).

III. DIRECT CURRENT BREAKDOWN STRENGTHS OF GASES/MIXTURES

A. Unitary Gases

Several new unitary gases were studied in this period. The DC breakdown voltage for 1,1,1-trichlorotrifluoroethane ($1,1,1\text{-C}_2\text{Cl}_3\text{F}_3$) was measured as a function of Pd at 150 torr and $T \approx 22^\circ\text{C}$; the results were shown earlier in Fig. 4. Plane-plane uniform field electrodes were used. The breakdown voltage relative to SF_6 is approximately 2.5. The 1,1,2- $\text{C}_2\text{Cl}_3\text{F}_3$ (Freon 113) isomer exhibits nearly the same relative breakdown strength under identical conditions. The present relative dielectric strengths of 2.5 are somewhat higher than the value of 2.1 obtained by Gockenbach.³¹ The boiling points of 1,1,1- $\text{C}_2\text{Cl}_3\text{F}_3$ and 1,1,2- $\text{C}_2\text{Cl}_3\text{F}_3$ are, respectively, 45°C and 48°C . No corrections for compressibility were made. However, approximate vapor pressures for these compounds were determined by allowing the liquid and vapor to come into equilibrium and measuring the pressure directly. We found that the 1,1,2- $\text{C}_2\text{Cl}_3\text{F}_3$ had a vapor pressure of at least 625 torr at 23°C and the 1,1,1- $\text{C}_2\text{Cl}_3\text{F}_3$ had a vapor pressure of not less than 345 torr at 21°C . Data were taken at 150 torr in an effort to avoid as much as possible compressibility problems.

The dielectric strengths of carbonyl sulfide (OCS) and 1,1,1- $\text{C}_2\text{H}_3\text{F}_3$ (1,1,1-trifluoroethane) have been measured using the new small breakdown test chamber with 3/8 in. diam sphere-sphere stainless electrodes (see Sect. VII for details). These data along with those for $\text{c-C}_4\text{F}_8$, SF_6 , and N_2 --taken under identical conditions for comparison--are shown in Fig. 10. The curvature at the higher electrode separations, d , is caused by the

Fig. 10. DC breakdown voltages, V_s , of OCS , $1,1,1\text{-CH}_3\text{CF}_3$, $c\text{-C}_4\text{F}_8$, SF_6 , and N_2 as functions of electrode separation, d , at $P = 500$ torr and $T \approx 22^\circ\text{C}$ (3/8 in. diam sphere-sphere geometry).

increasingly more nonuniform electric field. However, at lower gap separations the V_s versus d function is a straight line for all gases and estimates of the relative breakdown strengths can be made. These estimates are given in Table 6.

Great caution was taken in the measurement of the breakdown voltage of OCS, which is both highly toxic and explosive in the presence of oxygen. A small chamber with special shielding and gas exhaust system was made for investigating OCS and other potentially hazardous compounds. The study of OCS was motivated by a recent report³² which indicated that the total electron scattering cross section of this compound is large at low electron energies.

Table 6. Relative dielectric strengths of pure gases using the small breakdown test chamber

Gas	$(V_s)_R^a$
c-C ₄ F ₈	1.36
SF ₆	1.00
OCS	0.94
1,1,1-CH ₃ CF ₃	0.58
N ₂	0.53

^aObtained by averaging the ratios of the breakdown voltage of each gas to SF₆ at several gap settings in the linear region of the V_s versus d functions.

Figure 11 shows the DC breakdown voltages, V_s versus d for two additional pure gases, C₂ClF₅ (Freon 115) and 1-C₃F₆ (hexafluoropropene, $\begin{array}{c} \text{F} & \text{F} & \text{F} \\ | & | & | \\ \text{C}=\text{C}-\text{C}-\text{F} \\ | & & | \\ \text{F} & & \text{F} \end{array}$) compared with SF₆ and c-C₄F₈. The relative breakdown strengths

Fig. 11. DC breakdown voltages, V_s , of C_2ClF_5 and $1-C_3F_6$ compared to $c-C_4F_8$ and SF_6 at $P = 500$ torr and $T = 22^\circ C$ (plane-plane electrode geometry).

obtained from the slopes of the straight lines are given in Table 7. Hexafluoropropene captures electrons weakly.³³ It is considered to be a good electron thermalizing component gas to a multicomponent gaseous dielectric in combination with strong electron attaching additives.

Table 7. Relative breakdown strengths of pure gases
(P = 500 torr; T = 22°C; plane-plane electrode geometry)

Gas	Slope (kV/atm-mm)	Intercept (kV)	$(V_s)_R$
C ₂ ClF ₅ (Freon 115)	10.18	1.12	1.16
1-C ₃ F ₆	8.25	1.34	0.94
c-C ₄ F ₈	10.60	3.47	1.21
SF ₆	8.76	0.046	1.00

B. Gas Mixtures

(i) Binary Mixtures with One Electron Attaching and One Dipolar Component

We have continued our work on multicomponent gas mixtures containing dipolar components. Our data, summarized in Table 8 and Figs. 12 to 15, indicate that binary mixtures of dipolar and electron attaching gases exhibit pronounced synergism. Thus, CF₄ with a dipole moment, D, equal to zero does not exhibit synergism with either attaching gas SF₆ or c-C₄F₈, based upon the weighted average calculated according to partial pressure (or volume) and the relative strengths of the pure gases.* The dipolar gases CHF₃ (D = 1.65 debye), CH₂F₂ (D = 1.97 debye)

*It is noted that C₂F₆ which is also nonpolar exhibited a synergistic behavior in mixtures with SF₆ (ref. 18).

Table 8. Synergistic effects on dipolar electron attaching binary gas mixtures

SF ₆	c-C ₄ F ₈	2-C ₄ F ₅	CF ₄	CHF ₃	CH ₂ F ₂	1,1,1-CH ₃ CF ₃	Measured ^a (V _s) _R	Calculated ^b (V _s) _R
(Percent by volume)								
30			70				0.62	0.65
30				70			0.65	0.53
30					70		0.63	0.51
30						70	0.80	0.71
	30		70				0.70	0.71
	30			70			0.90	0.59
	30				70		0.90	0.57
	30					70	1.08	0.76
		30		70			1.23	0.89
		30			70		1.22	0.87
		30				70	1.36	1.07
100							1.00	
	100						1.19	
				100			0.33 ^c	
			100				0.50 ^d	
					100		0.3 ^e	
						100	0.58 ^f	

^aMeasured DC dielectric strength relative to SF₆ of 1, under identical conditions (plane-plane electrode geometry, 500 torr total pressure, T = 22°C).

^bWeighted average based on the percent by volume and relative strengths for pure gases.

^cFrom G. Camilli, and R. E. Plump, Trans. AIEE 72 Pt. I, 93 (1953).

^dFrom L. J. Berberich, C. N. Works, and E. W. Lindsay, Trans. AIEE 74 Pt. I, 664 (1955).

^eFrom E. E. Charlton and F. S. Cooper, General Electric Review 40, 438 (1937).

^fOur measurements made with 3/8 in. dian sphere-sphere electrodes at 500 torr total pressure.

Fig. 12. DC breakdown voltages, V_s , for mixtures of CF_4 and the attaching gases SF_6 and $\text{c-C}_4\text{F}_8$ as functions of electrode separation at 500 torr total pressure; $T \approx 22^\circ\text{C}$ (plane-plane electrode geometry).

Fig. 13. DC breakdown voltages, V_s , for mixtures of the dipolar gas CH_2F_2 ($D = 1.97$ debye) and the attaching gases 2- C_4F_6 , c- C_4F_8 , and SF_6 as functions of electrode separation, d , at 500 torr total pressure; $T \approx 22^\circ\text{C}$ (plane-plane electrode geometry).

Fig. 14. DC breakdown voltages, V_s , for mixtures of the dipolar gas CHF₃ ($D = 1.65$ debye) and the attaching gases 2-C₄F₆, c-C₄F₈, and SF₆ as functions of electrode separation, d , at 500 torr total pressure; $T \approx 22^\circ\text{C}$ (plane-plane electrode geometry).

Fig. 15. DC breakdown voltages, V_s , for mixtures of the dipolar gas 1,1,1- CH_3CF_3 and the attaching gases 2- C_4F_6 , c- C_4F_8 , and SF_6 as functions of electrode separation, d , at 500 torr total pressure; $T \approx 22^\circ\text{C}$ (plane-plane electrode geometry).

and 1,1,1- CH_3CF_3 ($D = 2.32$ debye) do exhibit synergism with each of the attaching gases SF_6 , $\text{c-C}_4\text{F}_8$, and 2- C_4F_6 as shown in Table 8.* These synergisms are consistent with our data (see Sect. VI C) using cylindrical geometry in which significant synergism with 1,1,1- CH_3CF_3 and the electron attaching gas $\text{c-C}_4\text{F}_8$ was observed and comparatively little (if any) synergism was noted with CF_4/SF_6 or $\text{CF}_4/\text{c-C}_4\text{F}_8$ mixtures.

(ii) Binary Mixtures of Electron Attaching and Electron Thermalizing or Electron Attaching Gases

Mixtures of C_2ClF_5 (Freon 115) and SF_6 have been studied systematically, and the results are shown in Fig. 16. We see a nearly linear increase in breakdown voltage as the percentage of C_2ClF_5 is increased. There is very slight, if any, synergism observed for these mixtures.

Two strongly electron attaching gases, $\text{c-C}_4\text{F}_8$ and SF_6 , were mixed to test for synergisms with the results given in Fig. 17. We observe a slight improvement over a 50% weighted average line that would bisect the two 100% curves. Further studies in which the emphasis is placed on electron attaching gases are planned.

The double bonded compound 1- C_3F_6 has been studied in binary mixtures with two strong electron scavengers, SF_6 and $\text{c-C}_4\text{F}_8$. Figures 18 and 19 give the breakdown voltages of these mixtures as functions of gap separation and percentages of component. Here we observe for the first time in any of our measurements a synergism such that the breakdown voltage of the mixture is higher than the breakdown voltage for either pure component. These measurements were all conducted at 500 torr total pressure with uniform field plane-plane electrode geometry.

* We did not measure the V_s of the 30% 2- C_4F_6 /70% CF_4 mixture since there were significant carbon deposit problems; hence entrees were not put in the table.

Fig. 16. DC breakdown voltages of mixtures of C_2ClF_5 (Freon 115) in SF_6 at 500 torr total pressure; $T \approx 22^\circ C$ (plane-plane electrode geometry).

Fig. 17. DC breakdown voltages of mixtures of two electron attaching gases, $c\text{-C}_4\text{F}_8$ and SF_6 , at 500 torr total pressure ($T \approx 22^\circ\text{C}$) (plane-plane electrode geometry).

Fig. 18. DC breakdown voltages of mixtures of 1-C₃F₆ and SF₆ at 500 torr total pressure (T ≈ 22°C) (plane-plane electrode geometry).

Fig. 19. DC breakdown voltages of mixtures of 1-C₃F₆ and c-C₄F₈ at 500 torr total pressure ($T \approx 22^\circ\text{C}$) (plane-plane electrode geometry).

The synergistic effects are much more pronounced at the larger gap spacings. The maximum synergisms occur at 60% 1-C₃F₆/40% SF₆ and 40% 1-C₃F₆/60% c-C₄F₈, which are shown in Fig. 20 as the ratio of the measured breakdown voltage to the breakdown voltage obtained from the linearly weighted average as a function of d . A higher synergistic effect is observed for the c-C₄F₈ mixtures than for the SF₆ mixtures.

Two additional mixture studies were conducted on the new, small breakdown test chamber. Figure 21 shows the DC breakdown voltages as functions of the percentage of c-C₄F₈ in 1,1,1-CH₃CF₃ for different gap settings using the 3/8 in. diam sphere-sphere electrodes. At a given gap separation we see a strong synergistic behavior as the percentage of c-C₄F₈ is increased. These preliminary results suggest that further investigation of the c-C₄F₈/1,1,1-CH₃CF₃ dielectric system is warranted.

The breakdown voltage of mixtures of OCS and SF₆ are presented in Fig. 22; for the higher gaps, (i.e., more nonuniform electric fields) we see pronounced synergism for which the mixture is again higher than either component alone. These synergistic effects may be related to the large electron scattering cross sections of OCS at low-electron energies.³²

Fig. 20. Ratio of the measured DC breakdown voltage to the breakdown voltage obtained from the linear weighted average for 1-C₃F₆ mixed with SF₆ and c-C₄F₈.

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Fig. 21. DC breakdown voltages of mixtures of $c\text{-C}_4\text{F}_8$ and $1,1,1\text{-CH}_3\text{CF}_3$ at 500 torr total pressure; $T \approx 22^\circ\text{C}$ (3/8 in. diam sphere-sphere electrodes).

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Fig. 22. DC breakdown voltages of mixtures of OCS and SF_6 at 500 torr total pressure; $T \approx 22^\circ C$ (3/8 in. diam sphere-sphere electrodes).

IV. ENVIRONMENTAL EFFECTS STUDIES

A. Initial Decomposition of Gaseous Dielectrics under Electron Impact

A study of the electron impact-induced fragmentation of the dielectric 1,1,1- $\text{C}_2\text{Cl}_3\text{F}_3$ (1,1,1-trichlorotrifluoroethane) has been made, employing the method of time-of-flight mass spectrometry. The results are shown in Fig. 23, which gives the negative ion intensity as a function of the collision energy of the impacting electron for the most intense ions Cl^- and F^- . Two additional, but weaker, fragment ions, Cl_2^- and CCl_3^- , were observed and are included in Table 9. In addition, the SF_6^{-*} resonance formed from collisions of thermal electrons with SF_6 is presented in Fig. 23 for comparison purposes. Since it has been shown that the SF_6^{-*} resonance at ~ 0.0 eV is much narrower than the resolution of the instrument,^{16,34} the shape of the SF_6^{-*} resonance is actually a measure of the electron energy distribution. By comparing the $\text{SF}_6^{-*}/\text{SF}_6$ resonance with the $\text{Cl}^-/1,1,1\text{-C}_2\text{Cl}_3\text{F}_3$ resonance, it can be seen that the Cl^- intensity decreases more slowly with increasing electron energy than the SF_6^{-*} intensity does, indicating the presence of additional unresolved resonances in the 0 to 1 eV energy region. This is certainly consistent with the swarm unfolded electron attachment cross sections presented in Sect. II A (Figs. 3 and 5). Consistent with the cross sections in Figs. 3 and 5, we found the peak of the Cl^- resonance to coincide with the SF_6^{-*} peak and to occur at ~ 0.0 eV from a calibration using the $\text{SF}_5^-/\text{SF}_6$ resonance, which is known to maximize at 0.37 eV.¹⁶

The F^- fragment ion is the next most abundant ion formed; however

Fig. 23. Negative ion intensity as a function of electron energy for Cl^- and F^- from $1,1,1-C_2Cl_3F_3$ and SF_6^{-*} from SF_6 .

Table 9. Fragment negative ions formed by low-energy electron impact on 1,1,1- $\text{C}_2\text{Cl}_3\text{F}_3$

Negative ion	Energy position of resonance maximum (eV)	Relative peak intensity at maximum
Cl^-	~ 0.0	1000
F^-	6.3	0.58
Cl_2^-	6.5-7.0	~ 0.05
CCl_3^-	6.5-7.0	~ 0.015

it is over a factor of 1000 weaker in intensity than the Cl^- ion. The primary peak in the F^- intensity curve is located at 6.3 eV. A second peak occurs at ~ 2.25 eV. The negative ion fragments Cl_2^- and CCl_3^- were barely observable, having maximum intensities a factor of ~ 10 and ~ 30 , respectively, smaller than the maximum F^- intensity. The resonance maxima for both Cl_2^- and CCl_3^- were in the 6.5 to 7.0 eV electron impact energy range. The weak intensity of Cl_2^- is consistent with the observation of Johnson et al.¹⁰ that for chlorine substituted hydrocarbons, the Cl_2^- ion intensity was "weak" when the two chlorine atoms in the parent molecule were originally bound to the same carbon atom. This is particularly true in the case of 1,1,1- $\text{C}_2\text{Cl}_3\text{H}_3$ for which Johnson et al.¹⁰ measured a Cl_2^- intensity ~ 2000 times smaller than the Cl^- ion intensity.

B. Prolonged Stress Effects

Eleven stress cells have been constructed and placed in operation during this reporting period.* A description of the cells is given in

*We are thankful to J. G. Carter for his assistance on this project.

Sect. VIII, and a schematic diagram is shown in Fig. 24. These cells are presently being used for testing SF_6 and $\text{c-C}_4\text{F}_8$ under various conditions of time, temperature, and voltage type (AC or DC) during prolonged periods of electrical stress. The gases will subsequently be analyzed by gas chromatography/mass spectrometry. Table 10 lists the various stress tests currently in progress.

Table 10. Conditions for long-term stress tests

Sample No.	Gas	Temp. ($^{\circ}\text{C}$)	Voltage	Time
1	SF_6	22	DC	3 months
2	SF_6	22	DC	6 months
3	SF_6	22	DC	1 year
4	SF_6	22	0	<i>a</i>
5	SF_6	23	AC	<i>a</i>
6	SF_6	100	0	<i>a</i>
7	SF_6	100	DC	<i>a</i>
8	$\text{c-C}_4\text{F}_8$	23	0	<i>a</i>
9	$\text{c-C}_4\text{F}_8$	23	DC	<i>a</i>
10	$\text{c-C}_4\text{F}_8$	100	0	<i>a</i>
11	$\text{c-C}_4\text{F}_8$	100	DC	<i>a</i>

^aTime will depend on the results of samples 1, 2, and 3.

Fig. 24. Schematic of prolonged-stress cells

C. Breakdown Product Analysis

We have previously reported that although the perfluorocarbon 2-C₄F₆ produces considerable black deposits on electrodes and containment walls of a spark chamber, mixtures of 2-C₄F₆ with SF₆ produce little or no black deposits following repeated sparking.¹⁸ This observation has prompted a systematic study of the manner in which gas mixtures decompose from arcing. Various concentrations of 2-C₄F₆ in SF₆ were prepared and sparked 3000 to 4000 times within a 1/4 liter stainless steel chamber. The electrodes were also stainless steel and spherically shaped. In all samples the total pressure was 1000 torr and the electrode gap separation was 1.0 mm. Breakdowns were produced by a capacitive discharge delivering ~0.5 joules per spark. The sparked gas was then transferred to a stainless container, which was subsequently filled to ~2 atms with helium. The addition of helium was required to facilitate the injection of the sparked gas sample into the helium carrier gas stream of a gas chromatograph. The injection was accomplished by releasing the sample gas/helium mixture into a short piece of tygon tubing. A syringe specifically used for gas sampling was injected through the tubing wall and samples ranging from 100 to 500 μ liter were withdrawn and then injected into a combined gas chromatography-mass spectrometry (GC/MS) system. In the GC a silicon gel column was utilized since it provided suitable separation of perfluorocarbons. As the sample gas eluted from the column a magnetic sector mass spectrometer swept a mass range of ~600 amu (atomic mass units) every three seconds. Data was then accumulated in the form of ion intensity as a function of scan number (effectively as a function of retention time). However,

since the column temperature was increased during a run (to provide better separation) the time scale is not linear and therefore number of scans is more appropriate for graphical presentation.

In interpreting the data there are two primary objectives: (a) identification of the components in a gas sample and (b) observation of the relative differences in ion intensities for a variety of gas samples. One of the difficulties in achieving (a) is that in a total ion chromatogram small product peaks may be swamped by a large nearby peak such as one due to a starting component (in this case SF_6 or $2\text{-C}_4\text{F}_6$). This is illustrated in chromatogram I of Fig. 25. [The sample is a sparked $2\text{-C}_4\text{F}_6$ (60%)/ SF_6 (40%) mixture.] The peak centered at scan 85 is quite broad and the mass spectrum at 85 indicates that this peak is primarily due to SF_6 . Also for scans above ~ 150 the ion intensity is so broad that specific peaks are nearly impossible to define. This sort of problem can be considerably alleviated by plotting the intensity of a specific ion as a function of scan number. Thus, a compound which does not possess that ion in its characteristic positive ion mass spectrum is effectively rendered "invisible" in that ion chromatogram. For example, chromatogram II in Fig. 25 is a plot of mass 69 (CF_3^+) as a function of scan number. It is readily seen that the peak identified as air in the total ion chromatogram* is entirely absent in the $m/e = 69$ chromatogram. In the $m/e = 69$ chromatogram no peak appears at scan 85, but rather there are two peaks at scans 80 and 90. The mass spectra taken at scans 80 and 90 revealed the presence of C_2F_6 and C_2F_4 respectively. Also, the peak at

*This is air which was introduced in the transfer by syringe of the gas sample into the GC/MS.

Fig. 25. Ion intensity versus number of scans for a sparked sample of 2-C₄F₆ (60%)/SF₆ (40%) injected into a GC/MS (see text for details of sample preparation). (I) Total ion intensity. (II) m/e = 69. (III) m/e = 95. (IV) m/e = 100. (V) m/e = 127. (VI) m/e = 169.

scan 160 identified as C_4F_{10} was well resolved in the $m/e = 69$ chromatogram but marginally resolved in the total chromatogram.

Chromatogram III in Fig. 25 is a plot of the mass 95 ion as a function of scan number. This ion is apparently an ion of a product species and is identified as S_2CF^+ . Two well defined peaks appear in this chromatogram and are centered at scans 199 and 253. These peaks are buried in the background of the total ion chromatogram. Tentative identifications based on the mass spectra taken at both scan 199 and 253 indicate a molecule with the molecular formula $S_2C_2F_4$. Both peaks yield nearly identical mass spectra except for the presence of a fairly strong line at 69 amu, indicating the formation of a CF_3^+ group. It is believed that the two compounds are isomers of each other; however there is insufficient information at present to determine the bonding arrangement of the two molecules. The broad peaks at scan 215 and 233 could not be identified. The compound eluting as scan 233 possesses a Cl^+ ion in its mass spectrum and appears to be a product formed in the discharge resulting from reactions with a chlorocarbon impurity.

The ion chromatogram IV in Fig. 25 is shown for $m/e = 100$ ($C_2F_4^+$). The compounds C_2F_6 , C_2F_4 , C_3F_8 , and C_4F_{10} are again observed, as they were in the CF_3^+ ion chromatogram. Since mass 100 is one of the most prominent lines in the mass spectrum of C_2F_4 (the most intense line occurring at 81 amu) the C_2F_4 peak in this ion chromatogram is intense. The background at scans greater than 150 is negligible, making it possible to observe the presence of C_4F_8 at scan 168.

The fifth (V) ion chromatogram is that of SF_5^+ ($m/e = 127$). Only one peak is observed and it occurs at scan 85. It is the peak responsible

for the broad structure centered at scan 85 in the total ion chromatogram (I) and was easily identified as one of the original components in the sample, namely SF_6 .

The ion chromatogram of C_3F_7^+ ($m/e = 169$) is plotted in VI. In addition to the previously observed C_3F_8 and C_4F_{10} compounds, the higher perfluorocarbons C_5F_{12} and C_6F_{14} were detected at scans 192 and 224 respectively.

In Fig. 26 a comparison is made of the ion chromatogram of CF_3^+ ($m/e = 69$) for various concentrations of 2- C_4F_6 in SF_6 following repeated sparking. The first (I) chromatogram labeled "BLANK" is a 50/50 mixture of 2- C_4F_6 and SF_6 without sparking. Aside from a trace amount of CF_4 , no perfluorocarbon was observed below scan ~145. An examination of a sparked sample of 80% 2- C_4F_6 in SF_6 reveals formation of the products CF_4 , C_2F_6 , C_2F_4 , and C_3F_8 . The successive chromatograms (II to V) are for decreasing amounts of 2- C_4F_6 in SF_6 in 20% decrements. The vertical scale gives the CF_3^+ ion intensity. It should be noted that the intensity scale is arbitrary and that the scales are different in all chromatograms. However, relative intensities of ion peaks may be compared for each chromatogram so that trends in product formation may be realized.

It can be seen, for example, that the CF_4 product (relative to 2- C_4F_6) increases dramatically as the amount of 2- C_4F_6 is decreased. This increase coincides with an increase in the partial pressure of SF_6 in the starting sample. Thus, it appears that there are reactions involving products of 2- C_4F_6 with SF_6 to produce an increased quantity of perfluoromethane (CF_4). Similar observations can be made for the other lower perfluorocarbons (C_2F_4 , C_2F_6 , and C_3F_8), but the increases are not as pronounced. It is

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Fig. 26. Intensity of CF_3^+ ($m/e = 69$) versus number of scans for various $2\text{-C}_4\text{F}_6/\text{SF}_6$ mixtures injected into a GC/MS. (See text for details of sparked sample preparation). (I) Unsparked 50/50 mixture. (II) $2\text{-C}_4\text{F}_6$ (80%)/ SF_6 (20%). (III) $2\text{-C}_4\text{F}_6$ (60%)/ SF_6 (40%). (IV) $2\text{-C}_4\text{F}_6$ (40%)/ SF_6 (60%). (V) $2\text{-C}_4\text{F}_6$ (20%)/ SF_6 (80%).

also observed that these relative concentrations reach a maximum for the 40/60 mixture of 2-C₄F₆/SF₆ and slightly decrease in the 20/80 mixture. We have noted previously that black deposits are almost entirely inhibited for the 40/60 mixture, suggesting a possible relationship between these two phenomena. Further work on this system will require quantitative data on final product formations and detection of intermediate products.

D. Preliminary Results with the Quadrupole Mass Spectrometer

The electron impact ionizer in this instrument is suited for the production of positive ions only because of its design. It is, however, extremely sensitive. Figure 27 is the positive ion mass spectrum of SF₆ using the electron impact ionizer. The SF₆ pressure in the ionizer was 1×10^{-6} torr, with 50 μ A of electron emission at 70 eV electron energy. The detection electronics were set to their least sensitive range. The predominant ion is SF₅⁺, followed by SF₃⁺, with traces of SF₄⁺, SF₂⁺, SF⁺, S⁺, and F⁺. There were also minor peaks due to H₂O⁺, N₂⁺, SF₂⁺⁺, and SF₃⁺⁺. There was no indication of SF₆⁺. This spectrum agrees well with published data.³⁵

Figure 28 is the mass spectrum for air using the high pressure spark ion source. The air was first dried by passing it through a tube packed with Linde 5A molecular sieve. The source pressure was 15 torr and the temperature was 100°C. The most predominant negative ion was O⁻ followed by C₂H₅O⁻ (from the solvent used to clean the ion source), O₂⁻, OH⁻, CN⁻, Cl⁻, NO₃⁻, and F⁻. The major positive ion was N₂⁺, followed in intensity by O₂⁺, Ar⁺, CO₂⁺, N⁺, O⁺, and H₂O⁺. The electrodes were made

Fig. 27. Positive ion mass spectrum of SF_6 using the electron impact ionizer at a pressure of 1×10^{-6} torr in the inlet chamber with 70 eV electron energy and 50 μA emission current.

Fig. 28. Negative and positive ion mass spectra of dry air using the high pressure spark ion source, at a pressure of 15 torr in the ion source, an electrode gap of 0.3 mm and an electrode-aperture of 1.24 mm.

of tantalum, the gap was set at 0.3 mm and the distance between the electrodes and the aperture was 1.24 mm. Further tests for the negative ions showed that the $\text{C}_2\text{H}_5\text{O}^-$ and NO_3^- ions were still visible at an electrode-aperture separation of 6 mm. The intensities of $\text{C}_2\text{H}_5\text{O}^-$ and NO_3^- did not fall off as rapidly with the electrode to aperture distance as did the intensities of the other negative ions.

Figures 29A and 29B are the negative and positive ion mass spectra of CF_4 taken with the spark ion source at a pressure of 16 torr. All other conditions were the same as for the air spectra. The major negative ion was F^- , followed by a peak at mass 39, then CF_3^- , CNO^- , CN^- , and Cl^- . The predominant positive ion was CF_3^+ , followed by CF_2^+ , CF^+ , CO_2^+ , N^+ (or CO^+), C^+ , F^+ , and O^+ . At these lower pressures, the discharge appeared more like a corona discharge rather than a spark, although the source was powered by a high voltage pulse power supply at a pulse repetition rate of about 500 Hz. The glow was not localized to the region between the two electrodes, but instead covered the high voltage electrode.

Figure 30 is the mass spectra for CF_4 , but at a source pressure of 270 torr. All other conditions were the same as for the two previous mass spectra (Figs. 28 and 29). In this case, however, the discharge glow was confined to the region between the electrode tips. A black deposit that appeared to be mostly carbon, though it was not analyzed, was observed coating the aperture disc at the completion of the experiment. The negative ion spectrum was simple, showing only F^- and possibly the same peak at mass 37 as in the lower pressure mass spectrum. This peak has not been positively identified, although a possible candidate is HF_2^- . Further work is needed before any final conclusions can be drawn. The positive ion

Fig. 29. Negative and positive ion mass spectra of CF_4 using the high pressure spark ion source, at a pressure of 15 torr in the ion source, an electrode gap of 0.3 mm, and an electrode-aperture separation of 1.24 mm.

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Fig. 30. Negative and positive ion mass spectra of CF_4 using the high pressure spark ion source at a pressure of 270 torr in the ion source, an electrode gap of 0.3 mm, and an electrode-aperture separation of 1.24 mm.

spectrum was dominated by CF_3^+ , CF_2^+ , and CF^+ , with traces of CO_2^+ and N_2^+ or CO^+ . The noise for these spectra was considerably greater than in the spectra taken at lower source pressures.

The next gas examined was SF_6 (dried by passing it through a column packed with Linde 5A molecular sieve). The source pressure was maintained at 25 torr and the temperature fixed at 100°C . The only ion observed-- in either the positive or the negative mode of operation-- was F^- . This result is very interesting in light of the work of Lowke and Lieberman³⁶, who calculated that F^- would be more abundant than electrons or other negative ions below an arc temperature of 4500°K . At a source pressure of 300 torr, no ions were observed.

The behavior of SF_6 in the ion source is dependent on the amount of moisture in the source. Previous experiments with SF_6 straight from the gas cylinder and an unbaked ion source resulted in considerable liquid and solid deposits on the aperture and the electrodes.

Further experiments will emphasize primarily SF_6 , since this gas is currently of great commercial and practical interest.

E. Sulfur Hexafluoride Breakdown Products (Literature Review)

(i) Chemistry of Sulfur Fluorides

Five sulfur fluorides, SF_2 , S_2F_2 , SF_4 , SF_6 , and S_2F_{10} , are known.³⁷ In addition, there are several sulfur oxy-fluorides, including SOF_2 , SO_2F_2 , SOF_4 , and $\text{S}_2\text{F}_{10}\text{O}$.

Sulfur hexafluoride is a chemically inert gas with low toxicity.³⁸ However, between 500 and 600°C , SF_6 starts to decompose into SF_4 and SF_2 .³⁹

The structure of SF_6 is a symmetric octahedron of symmetry O_h with no electric dipole moment.

Sulfur tetrafluoride (SF_4) is a highly toxic and corrosive gas.³⁸ It is rapidly hydrolyzed by traces of moisture, forming hydrofluoric acid (HF) and thionyl fluoride (SOF_2). The structure of SF_4 is a trigonal bipyramid with C_{2v} symmetry.

Sulfur difluoride (SF_2) is an unstable compound, which decomposes rapidly into sulfur, sulfur tetrafluoride, and disulfur difluoride.⁴⁰ It readily reacts with traces of moisture.⁴¹

Disulfur difluoride (also known as sulfur monofluoride; S_2F_2) is also thermally unstable and rapidly hydrolyzes when exposed to traces of moisture.⁴¹ It readily attacks glass and quartz at room temperature. There are two isomers of S_2F_2 , the first of which, (SSF_2), contains sulfur in two valence states, 2 and 4.⁴² The second isomer has a nonpolar (FSSF) structure,⁴³ which rearranges to the first isomer at room temperature with a 15 min first-order half-life. The two isomers exhibit slightly different mass spectra.⁴³

Disulfur decafluoride (also known as sulfur pentafluoride; S_2F_{10}) is a highly toxic gas, and is a contaminant in freshly prepared SF_6 .³⁹ It is carefully removed from the SF_6 before it is sold. It is not readily hydrolyzed by traces of moisture, but it does decompose when heated above 300°C , forming principally SF_4 and SF_6 .⁴⁴ The structure of S_2F_{10} is two square pyramids, each being a sulfur with five fluorine atoms, joined between the two sulfur atoms, belonging to symmetry group D_{4d} .⁴⁵

(ii) Thermal Effects in SF_6

The equilibrium concentrations of the thermal decomposition products

for a starting mixture of 1 mole % SF_6 and 99 mole % Ar have been calculated over the temperature range from 1000 to 3500°K.⁴⁶ From 1000 to 1500°K, SF_6 dissociates principally into SF_4 . In the region from 1500 to 2000°K, the major products are SF_4 and SF_3 . Finally, above 2000°K, SF_6 dissociates primarily into SF_2 and SF.

When SF_6 is heated to 1500°C in a carbon Knudsen cell and the products passed into an electron impact mass spectrometer, the following ions are detected:⁴⁷ S^+ , S_2^+ , SF^+ , SF_2^+ , SF_3^+ , SF_4^+ , SF_5^+ , CF_2^+ , CS^+ , CS_2^{2+} , and SCF_2^+ . The authors⁴⁷ inferred the neutral precursors to these ions to be S, S_2 , SF, SF_2 , SF_4 , SF_6 , CF_2 , CS, CS_2 , and SCF_2 on the basis of their positive ion appearance potentials.

(iii) Ions and Ion-Molecule Reactions in SF_6

There has been considerable interest in the production and reaction of both the positive and negative ions in SF_6 . The principal negative ions formed by electron bombardment of SF_6 are SF_6^- , SF_5^- , F_2^- , and F^- .⁴⁸ The principal positive ions produced under electron impact at 70 eV electron energy are SF_5^+ and SF_3^+ , with traces of SF_4^+ , SF_2^+ , SF^+ , S^+ , and F^+ . The parent positive ion, SF_6^+ , is not observed.³⁵

Some work has been done concerning negative ion-molecule reactions in SF_6 .^{49,50} The most important reactions, in the pressure range of 1 to 50 torr, were found to be:

Reactions (1), (2), and (3) are all endoergic, based on the accepted values of the electron affinities of the various species involved and

the dissociation energies. For these reactions to occur, therefore, the reactant species must have significant kinetic energy to overcome these energy barriers.

In addition, work has been done on positive and negative ion recombination in SF_6 .⁵¹ The binary ionic recombination coefficients, α , have been measured for the following reactions:

Work has also been done on positive ion-molecule reactions in S_2F_2 .⁵² The rate constant for the highest yield process,

was estimated to be $2 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.

From this data, McGeehan et al.⁵⁰ concluded that SF_6^- would be the principal negative ion in high pressure cold discharges, and that F^- would predominate in a hot high pressure plasma. This agrees with the conclusions of Lowke and Liebermann³⁶ that, below about 4500°K, F^- ions are more abundant than electrons and drastically reduce the electrical conductivity of the arc. At these temperatures, the mole fraction of negative ions at the center of the arc is negligible, but there can be a considerable concentration of negative ions in the cooler outer region of the arc.

(iv) Decomposition of SF_6 in Electrical Discharges

The first report on the effects of arc discharges in SF_6 was by Schumb, Trump, and Priest.⁴¹ The SF_6 gas was contained in a 1 liter Pyrex round bottom flask, which was first evacuated for 24 hr to a pressure of 5 μ . The SF_6 was admitted to the flask through two

columns, the first containing KOH pellets to remove acid impurities, and then BaO to remove moisture. The final pressure was slightly above 1 atm. The electrodes consisted of an aluminum plate and eight stainless steel points. A corona was produced with currents from 50 to 200 mA, lasting from 50 to 200 hr. Decomposition products were produced, some of which could be absorbed by a 30% KOH solution and some which were not absorbed by the solution which possessed oxidizing properties. No further attempts to analyze the products were made. The authors concluded, on the basis of this evidence, that the products were lower fluorides of sulfur.

Camilli, Gordon, and Plump³⁹ performed a similar experiment in a 6 cubic foot steel tank with copper rods of 2 in. diam separated by 0.5 in. as electrodes. An arc with an initial voltage of 5 kV rms and a peak current of 8,000 A was applied. Infrared spectra of the resulting gases indicated the presence of SF₂, SF₄, and traces of CO₂, H₂S, and HF. No S₂F₁₀ was detected.

Edelson, Bieling, and Kohman⁵³ stressed SF₆ under three different sets of conditions. Their test chamber consisted of a gold plated metal tube with potassium bromide windows at either end sealed by rubber gaskets. The discharge was struck between the wall of the chamber and an electrode with a steatite insulator sealed by wax. The resulting decomposition products were detected by placing this chamber in the sample region of an infrared spectrophotometer. Under a high current 60-Hz arc, SF₂ was the major product, with a trace of SOF₂. Under the conditions of an electrodeless RF discharge using a high frequency spark coil as the power source, S₂F₂ was the only lower fluoride of sulfur detected.

Finally, exposure to electrical stress slightly below the corona point applied for a period of one year resulted in no detectable change in the dielectric.⁵³

A simple mass spectrometer experiment was performed by Thorburn.⁵⁴ A 30 cc glass discharge tube with point-point tungsten electrodes and a 1.3 cm gap was connected to the ion source of a conventional magnetic mass spectrometer with electron impact ionization. The pressure of SF_6 was ~ 0.5 atm. The first discharge was run at 0.4 mA with a pulse frequency of about once a second for 15 min. No appreciable change was observed for the positive ion abundances compared to unsparked SF_6 . The second discharge was run at 60 mA (at a frequency of once per second) for 2 hrs. There was an increase in the F^+ current, as well as the appearance of traces of SiF_4^+ , SiF_3^+ , and SO_2^+ . The third discharge was run at 10 mA for 30 min (also at a frequency of once per second), again resulting in an increase in the F^+ peak and the SF_2^+ peak. No separation of the decomposition products was attempted.

Leeds et al.⁵⁵ experimented with SF_6 as the insulating gas in a commercially sized circuit breaker, under varying conditions. They successfully interrupted currents of over 7,500 A, rms, at 132 kV. Activated alumina was found to be satisfactory in absorbing any decomposition products. No tests were made to determine what these products might be.

Manion, Philosophos, and Robinson⁵⁶ ran arc stability tests of various electronegative gases. The discharge cell was pyrex with a volume of 240 cc. The arc electrodes were made of copper and were water cooled, and the gap was set to 0.10 in. The arc was initiated with a manually

operated wiping rod. The initial SF_6 pressure was 1 atm. This test cell was connected directly to the inlet system of a conventional electron impact ionization mass spectrometer. The SF_6 was arced for 30 min at 0.75 A. There was a 30% decomposition of the SF_6 , but the dielectric strength remained unchanged. On the basis of the ions found, the presence of significant amounts of SOF_2 , SiF_4 , and S_2F_2 was deduced. Subsequent experiments with SF_4 revealed that it reacts with the glass container to form SOF_2 and SiF_4 at ambient temperature. The authors inferred that SF_4 was produced in arcing SF_6 , but that it reacted with the cell to form SiF_4 and SOF_2 before the cell contents could be analyzed. No separation of the decomposition products was attempted.

Gerasimov and Sidorkina⁵⁷ performed some experiments with gas mixtures containing SF_6 and air, using a 10 kV at 500 W arc. Analysis was by infrared spectrum. They reported SOF_4 and SO_2F_2 as the breakdown products.

Miyamoto et al.⁵⁸ and Miyamoto and Kamatani⁵⁹ did some experiments on SF_6 using a time-resolved mass spectrometer, with a miniature arc chamber attached to the ion source. Among the products reported were F_2^- , SOF , SF_2 , and SO_2F_2 . The SO_2F_2 was found only when large amounts of H_2O were injected.

A general review of SF_6 , its use in electrical equipment, and its decomposition are contained in a paper by Hudson,⁶⁰ covering the period up to 1967.

Becher and Massonne⁶¹ carried out a series of experiments very similar to that of Edelson et al.⁵³ The test cell was the same, except for the silver electrode. Among the products detected by their infrared

spectra were S_2F_{10} and $S_2F_{10}O$ (in small quantities), as well as SF_4 , SOF_2 , SOF_4 , CF_4 , and SiF_4 .

Ermel⁶² performed a series of tests with mixtures of SF_6 and N_2 . A discharge chamber was connected directly to a mass spectrometer. An 80% N_2 /20% SF_6 gas mixture at ~ 1 atm pressure was exposed to a 10 mA AC spark (4.5 kV) for 15 min. The mass spectrum showed only nitrogen oxides (from O_2 impurities), NF_3 , and N_2F_2 . No separation of the decomposition products was attempted.

Hirooka et al.⁶³ used a ^{19}F nuclear magnetic resonance spectrometer to analyze SF_6 decomposition products, eliminating the necessity for separating the products for unambiguous analysis. The gas was contained in a steel cylinder with copper-tungsten alloy electrodes, and the pressure before sparking was 1 atm. A 9.2 kV at 30 kA AC arc was applied 10 times and then the SF_6 was analyzed. When the test vessel was dried before the SF_6 was added, the products were WF_6 , SF_4 , S_2F_2 , SOF_2 , SF_6 , COF_2 , CF_4 , and SiF_4 . The COF_2 was probably formed by the reaction of the gases with the organic sealing material in the vessel. When the cell was not dried before the SF_6 was added, the products were WF_6 , SOF_2 , SF_6 , SO_2F_2 , CF_4 , $Si(CH_3)_2F_2$, SiF_4 , and HF . The $Si(CH_3)_2F_2$, identified by gas chromatography-mass spectrometry, was probably formed by reaction with the vacuum grease.

Bartakova et al.⁶⁴ performed several experiments with SF_6 , including continuous AC discharge, corona discharge, and a DC spark discharge. Analysis was accomplished using a gas chromatograph. Among the products observed were SF_4 , SOF_2 , SO_2F_2 , SOF_4 , S_2F_2 , and S_2F_{10} . Also included in this article is a scheme for the production of all these species.

Diebold and McFadden⁶⁵ used traces of SF_6 in a microwave discharge to enhance the signal to noise ratio in electron paramagnetic resonance (EPR) spectroscopic studies of electrical discharges. When the SF_6 was added directly to the microwave or hollow cathode discharges in helium (to the extent of 0.5% SF_6), atomic sulfur was detected by the EPR.

(v) Discussion

A brief summary of the results of the decomposition of SF_6 in discharges is given in Table 11. There are three tentative conclusions that can be drawn from this data.

1. All the possible sulfur fluorides, SF_2 , S_2F_2 , SF_4 , and S_2F_{10} , can be produced in an arc discharge. The relative ratios of intensities will vary depending on the nature of the discharge and the power in the discharge.
2. The reaction products, or the reaction mechanism itself, are extremely sensitive to traces of moisture, either in the apparatus or in the SF_6 gas itself.
3. The presence of silica, glass, quartz, organic greases or sealing agents, or silicone rubbers, or any other materials which can be fluorinated, will also affect the decomposition products.

The first conclusion is drawn mainly from the data concerning the production of SF_2 and S_2F_2 . Under the milder conditions, such as the RF electrodeless discharge⁵³, S_2F_2 was a significant product. Under more severe conditions,³⁹ however, SF_2 was more abundant.

The susceptibility of the reaction product intensities to the presence of moisture is not at all surprising in view of the well known sensitivity of SF_4 ,³⁸ SF_2 , and S_2F_2 ^{38,41} to moisture.

Table 11. Reported decomposition products of SF₆ containing only S, F, O, and H atoms

Products	Discharge	Detection method	Reference
SF ₂ , SF ₄ , HF	AC arc	Infrared spectrum	39
SF ₂ , SOF ₂	AC arc	Infrared spectrum	53
S ₂ F ₂	RF discharge	Infrared spectrum	53
SOF ₄ , SO ₂ , F ₂	AC arc	Infrared spectrum	57
SO ₂ F ₂ , SOF, SOF ₂	Spark	Mass spectrum	59
SF ₄ ^a , SOF ₂ , S ₂ F ₂	DC arc	Mass spectrum	56
S ₂ F ₁₀ , S ₂ F ₁₀ O, SF ₄ , SOF ₂ , SOF ₄	AC arc	Infrared spectrum	61
SOF ₂ , SO ₂ F ₂ , H ^b	AC arc	Nuclear magnetic resonance	63
SF ₄ , S ₂ F ₂ , SOF ₂ ^c	AC arc	Nuclear magnetic resonance	63
SF ₄ , SOF ₂ , S ₂ F ₂	AC arc	Gas chromatograph	64
SF ₄ , SOF ₂ , SOF ₄ , S ₂ F ₁₀	Corona	Gas chromatograph	64
SF ₄ , SOF ₂ , S ₂ F ₁₀	Spark	Gas chromatograph	64
S	Microwave discharge	Electron paramagnetic resonance	65

^aPresence of SF₄ inferred from presence of SOF₂ and SiF₄ on the basis of behavior of SF₄ with traces of moisture.

^bReaction vessel not dried before use.

^cReaction vessel not dried before use.

The problem of reaction between components of the test vessel and the reaction products is not surprising either, considering the chemistry of the lower sulfur fluorides. For instance, SF_4 is used commercially for the synthesis of fluorinated products unavailable by more conventional methods,³⁸ since SF_4 is capable of replacing oxygen with fluorine in many organic, inorganic, and organometallic compounds.

It is clear that the decomposition of SF_6 in an electrical discharge is a complex process. Slight differences in conditions can significantly change the outcome of experiments. It is therefore necessary, for results to be composed in a realistic fashion, that conditions be reproduced exactly. Examples of such conditions are the nature of the discharge (corona, AC arc, DC arc, etc.), the power dissipated in the arc, the duration of the discharge, the gas pressure, the electrode geometry, the ratio of test cell volume to surface area, the average temperature of the gas, etc.

The effect of the analysis method on the test results must be considered. Conventional mass spectroscopy, infrared spectroscopy, nuclear magnetic and electron paramagnetic resonance spectroscopy, and gas chromatography all require a time lag between the stressing of the sample and the actual analysis. Because of the high reactivity of some of the products involved, this time lag may introduce changes in the amounts of various products detected. More sophisticated analytical techniques, such as atmospheric pressure ionization mass spectroscopy (where ions are produced in a region at one atmosphere pressure and are sampled through a very small orifice directly into the mass spectrometer) eliminate this difficulty. These other techniques are also better suited to the study

of the decomposition mechanisms involved since they allow the processes to be monitored while they are occurring, rather than limiting information to the nature of the final products.

The contamination of the gas by traces of water vapor must be carefully controlled. This will require vacuum baking of all components that come into contact with the gas, as well as the careful drying of the gas sample itself. The choice of test cell materials must also be made with care. Clearly, glass, quartz, steatite, rubbers, epoxy, etc., are unsuitable for this application. The metals copper, aluminum, and stainless steel appear satisfactory, as does aluminum oxide as an insulator or a viewing window. Teflon or kel-F, while supposedly inert to attack by the fluorides involved, might present a problem. Teflon is sometimes slightly porous and might contain a significant quantity of trapped water. Furthermore, if the teflon should become directly exposed to the discharge, it might decompose slightly, causing interference with the results, particularly if fluorocarbon gases are being studied. In general, then, the practices and procedures should be the same as those used in ultra-high vacuum work.

It is realized that many of these precautions are not possible in the practical commercial applications of these gases. In particular, the need for vacuum baking of the system would be impossible. These precautions are not necessarily needed in using the gases as dielectrics, but for studying the processes involved. Once the basic mechanisms are understood, the effects of more practical conditions can be studied. Hopefully, the deliberate inclusion of specific impurities into the gas or gas mixture might significantly improve its properties, particularly

with regard to the elimination of undesirable decomposition products.

A practical example of this is the use of SF_6 and/or CO_2 with halogenated alkanes to inhibit carbon formation.⁶⁶

Although many of the perfluorocarbon gases hold great promise as insulators, the study of SF_6 remains of central importance. The commercial use of SF_6 is widely established, unlike the use of perfluorocarbons. Furthermore, it is very possible that SF_6 will find even greater use in mixtures with other gases.

F. Toxicity of $2\text{-C}_4\text{F}_8$

The dielectric gas $2\text{-C}_4\text{F}_8$ had been tested by Dr. H. Witschi of the Biology Division for toxicity, and the results were reported in our last report (Appendix D).¹⁸ The tests showed that 24 hr exposure to mice proved to be fatal while 8 hr exposure was not. It was recently noted⁶⁷ that since no cold trap was used in the 24 hr test, the deaths might be due to impurities. For this reason the 24 hr test was re-run with a cold trap, and the report of this test is given in Appendix D. The results were the same as for the original test. The dramatic difference in toxicity between 8 and 24 hr exposure times is worth noting and could be due to some threshold effect.

V. IMPULSE STUDIES

In this period, we have extended our studies of the lightning impulse breakdown to mixtures of $c\text{-C}_4\text{F}_8$, SF_6 , and N_2 . Table 12 lists the V_{50} (voltage where breakdown is 50% probable) values and the V_{NO} (no breakdown in ten successive impulses) and V_{10X} (ten consecutive breakdowns) for a series of gas mixtures and gap settings for "point"-plane electrode geometry (the point is a 30° cone with a 1 mm radius on the end to prevent sparking from changing the geometry of the point). Note that the polarities stated in our last report¹⁸ were the reverse from the true impulse polarities.

These measurements show that for *negative* polarity at the point, the addition of $c\text{-C}_4\text{F}_8$ substantially increases the V_{50} values for a mixture. At 3 atm total pressure 40% $c\text{-C}_4\text{F}_8$ /60% N_2 is substantially better than pure SF_6 while 40% SF_6 /60% N_2 is substantially worse. A 5% $c\text{-C}_4\text{F}_8$ /35% SF_6 /60% N_2 mixture is almost as good as pure SF_6 and is $\sim 30\%$ better than 40% SF_6 /60% N_2 . Therefore, a small addition of $c\text{-C}_4\text{F}_8$ has a disproportionately large beneficial effect. A 20% $c\text{-C}_4\text{F}_8$ /80% SF_6 mixture at 3 atm total pressure has approximately a 50% higher V_{50} value than does pure SF_6 .

For *positive* polarity, however, $c\text{-C}_4\text{F}_8$ decreases the V_{50} values. At 3 atm total pressure with N_2 , any percentage of $c\text{-C}_4\text{F}_8$ from 5% to 40% gives a V_{50} value at 0.750 in. gap very close to 8 kV. Without N_2 the V_{50} values improve. For 20% $c\text{-C}_4\text{F}_8$ /80% SF_6 , 3 atm total pressure and 0.750 in. gap, V_{50} is 10.2 kV and still increasing, while V_{50} for pure SF_6 is 12.0 kV (see ref. 18) but is constant (within error bars)

Table 12. V_{50} , V_{NO} and V_{10X} for gas mixtures for various
electrode separations and polarities^a

Gas or gas mixture (pressure in torr)	Electrode separation (inches)	V_{50}^b (kV)	V_{NO}^c (kV)	V_{10X}^d (kV)	Polarity
c-C ₄ F ₈ (760)	0.375	7.2	5.5	8.0	+
	0.500	8.6	7.5	9.0	+
	0.625	9.2	8.0	10.5	+
	0.750	10.0	9.0	11.0	+
	0.875	10.5	9.0	11.5	+
c-C ₄ F ₈ (760)	0.375	7.3	5.5	8.0	-
	0.500	8.7	6.5	9.5	-
	0.625	10.7	8.0	11.0	-
	0.750	12.7	9.0	13.0	-
	0.875	14.8	10.0	15.5	-
c-C ₄ F ₈ (912) N ₂ (1368)	0.250	8.2	7.0	8.5	-
	0.375	11.7	8.0	12.0	-
	0.500	>15.5	>15.5		-
c-C ₄ F ₈ (912) N ₂ (1368)	0.500	7.0	6.5	8.0	+
	0.625	7.4	7.0	8.0	+
	0.750	7.8	7.5	8.5	+
	0.875	8.4	7.5	9.0	+
c-C ₄ F ₈ (608) N ₂ (912)	0.500	6.75	6.0	7.5	+
	0.625	7.25		8.0	+
	0.750	7.9	7.5	8.5	+
	0.875	8.25	7.5	9.0	+
c-C ₄ F ₈ (608) N ₂ (912)	0.250	6.25	6.0	7.0	-
	0.375	8.4	7.0	9.0	-
	0.500	10.8	9.5	11.5	-
c-C ₄ F ₈ (304) N ₂ (456)	0.500	6.75	6.5	7.0	-
	0.625	8.4	7.0	9.0	-
	0.750	9.9	9.0	10.5	-
	0.825	11.4	10.5	12.0	-
c-C ₄ F ₈ (304) N ₂ (456)	0.625	6.7	6.0	7.5	+
	0.750	7.3		8.0	+
	0.875	7.5	7.0	8.5	+
c-C ₄ F ₈ (456) SF ₆ (456) N ₂ (1368)	0.375	6.5	6.0	7.0	+
	0.500	7.2	6.5	8.0	+
	0.625	7.7	7.0	8.5	+
	0.750	8.2	7.0	9.0	+
	0.875	8.7	7.5	9.0	+
c-C ₄ F ₈ (456) SF ₆ (456) N ₂ (1358)	0.250	7.75	7.0	8.0	-
	0.375	10.8	10.0	11.5	-
	0.500	14.25	13.5	15.0	-
	0.625	18.0	17.0	19.0	-
	0.750	21.9	20.5	22.5	-
c-C F (304) SF ₆ (304) N ₂ (912)	0.375	7.6	7.0	8.0	-
	0.500	9.9	9.0	10.5	-
	0.625	12.25	11.5	12.5	-
	0.750	14.6	14.0	15.0	-
	0.875	17.0	16.5	18.0	-

Table 12 (continued)

Gas or gas mixture (pressure in torr)	Electrode separation (inches)	V_{50}^b (kV)	V_{NO}^c (kV)	V_{10X}^d (kV)	Polarity
c-C ₄ F ₈ (304)	0.500	6.8	6.0	7.5	+
SF ₆ (304)	0.625	7.5	6.5	8.0	+
N ₂ (9.2)	0.750	8.1	7.0	9.0	+
	0.875	8.75	7.5	9.5	+
c-C ₄ F ₈ (114)	0.500	7.1	6.0	7.5	+
SF ₆ (798)	0.625	7.5	6.5	8.5	+
N ₂ (1368)	0.750	8.0	7.0	8.5	+
	0.875	8.4	7.0	9.5	+
c-C ₄ F ₈ (114)	0.250	7.2	6.5	7.5	-
SF ₆ (798)	0.375	10.2	7.5	11.0	-
N ₂ (1368)	0.500	13.5	11.0	14.5	-
	0.625	17.0		18.0	-
	0.750	20.0	18.5	21.0	-
c-C ₄ F ₈ (76)	0.375	7.2	6.5	8.0	-
SF ₆ (532)	0.500	9.3	8.0	10.0	-
N ₂ (912)	0.625	11.2	10.0	12.0	-
	0.750	13.75	12.0	14.5	-
	0.875	16.0	14.5	17.0	-
c-C ₄ F ₈ (76)	0.625	7.7	6.5	8.5	+
SF ₆ (532)	0.750	8.3	7.0	9.0	+
N ₂ (912)	0.875	8.6	7.5	9.5	+
c-C ₄ F ₈ (456)	0.250	6.8	6.0*	8.0	+
SF ₆ (1824)	0.375	7.8	7.0	9.0	+
	0.500	9.0	7.5	9.5	+
	0.625	9.4	8.5	10.5	+
	0.750	10.2	9.0	11.0	+
	0.875	10.7	9.5	11.5	+
c-C ₄ F ₈ (456)	0.250	9.75	8.5	10.5	-
SF ₆ (1824)	0.375	14.3	10.5	15.0	-
	0.500	19.0	17.5	20.0	-
c-C ₄ F ₈ (304)	0.250	6.8	6.5	7.5	-
SF ₆ (1216)	0.375	9.8	8.0	10.5	-
	0.500	12.8	11.5	13.5	-
	0.625	16.25	14.0	16.5	-
	0.750	19.2	18.0	20.0	-
	0.875	22.8	21.5	23.5	-
c-C ₄ F ₈ (304)	0.375	7.7	6.5	9.0	+
SF ₆ (1216)	0.500	9.2	7.5	10.0	+
	0.625	10.2	8.5	11.5	+
	0.750	11.1	9.0	12.5	+
	0.875	12.0	10.0	14.0	+
c-C ₄ F ₈ (152)	0.500	7.3	6.0	8.0	+
SF ₆ (608)	0.625	8.4	7.0	9.5	+
	0.750	9.5	7.5	10.5	+
	0.875	11.25	8.0	12.5	+
c-C ₄ F ₈ (152)	0.500	6.75	6.0	7.0	-
SF ₆ (608)	0.625	8.2	7.0	8.5	-
	0.750	9.4	8.5	10.0	-
	0.875	11.2	10.0	11.5	-

Footnotes to Table 12.

^aThe rise time of the impulse is 1.2 μ sec, and the decay time to 0.5 of peak value is 50 μ sec. The electrode geometry was "point"-plane.

^b V_{50} value uncertainties are approximately ± 0.5 kV.

^c V_{N0} is the lower limit for ten consecutive impulses with no breakdown.

^d V_{10X} is the voltage of which ten consecutive breakdowns occurred.

for all gaps between 0.375 in. and 0.750 in. The present test chamber is not designed for gaps larger than 1 in. so no measurements for larger gaps, where V_{50} values for pure SF_6 and the mixtures with $\text{c-C}_4\text{F}_8$ would be expected to cross, have been made.

An example of what we expect at larger gaps is seen in the 20% $\text{c-C}_4\text{F}_8$ /80% SF_6 mixture at 2 atm total pressure. Here the V_{50} value at 0.875 in. gap is the same as the V_{50} value for pure SF_6 at 2 atm. Again the slope of V_{50} for the mixture as a function of gap is positive while the slope of V_{50} for pure SF_6 is almost zero.

Thus, the 20% $\text{c-C}_4\text{F}_8$ /80% SF_6 mixture appears to be very promising and further studies with sphere-sphere electrodes and with switching impulses are planned.

VI. APPLIED STUDIES

A. Cylindrical Geometry Testing

Studies of the electron attaching gases SF_6 , $\text{c-C}_4\text{F}_8$ (perfluorocyclobutane) and $2\text{-C}_4\text{F}_8$ (perfluorobutene-2), and their binary mixtures with the electron moderating gases CF_4 (carbon tetrafluoride) and $1,1,1\text{-C}_2\text{F}_3\text{H}_3$ (1,1,1-trifluoroethane)--besides N_2 --have begun in the practical test facility with concentric cylinder geometry. This apparatus has been described in detail previously.^{68,69} During this period, the breakdown strengths of the binary mixtures of the aforementioned electron attaching gases with CF_4 have been tested with the concentric cylinder geometry. Also, the effects of surface roughness of the inner electrode have been investigated.

After our breakdown tests with CF_4 were completed using the "old" power supply and chamber, a "new" power supply and a "new" chamber were installed. The new chamber has been fabricated, and it has been installed with the new Delta Ray high voltage power supply. With this chamber we are capable of using pressures up to ten atmospheres. The chamber is described under Apparatus (Sect. VIII). The electrodes were the same as those described previously.^{68,69} The breakdown voltages of SF_6/N_2 mixtures were measured with the 0.75-cm radius stainless steel smooth inner electrode, and the results were compared with the data taken with the old power supply and old chamber. It can be seen from Fig. 31 that there is a slight difference between the two sets of data. Below ~60 kV the breakdown voltages taken with the new power supply are higher, and

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Fig. 31. Breakdown voltages for SF₆/N₂ mixtures with cylindrical electrode radii of 0.75 and 2 cm inner electrode at negative polarity. (X) Data taken from new power supply and chamber; (O) data taken from old power supply and chamber.

above ~ 60 kV they are lower, than those taken with the old power supply. The new data are taken to be the correct ones, the deviation being due to the old power supply; these deviations do not affect past conclusions on the relative dielectric strength of gaseous dielectrics.

The breakdown strengths of the binary mixtures of $c\text{-C}_4\text{F}_8/1,1,1\text{-C}_2\text{F}_3\text{H}_3$ have been tested with the new chamber and power supply. All tests so far were made at 1 atm total pressure and ambient temperature ($\sim 22^\circ\text{C}$).

B. Cylindrical Geometry Breakdown Tests with CF_4 as the Moderator

The breakdown voltages of SF_6/CF_4 , $c\text{-C}_4\text{F}_8/\text{CF}_4$, and $2\text{-C}_4\text{F}_8/\text{CF}_4$ mixtures with a 0.75-cm smooth inner electrode at negative and positive polarities are presented in Figs. 32 and 33, respectively. In these figures, each data point is the mean of at least ten breakdowns with random scatter (standard deviation $\div$ mean) of less than 3%. As expected, the breakdown strengths of the mixtures decrease in the order $2\text{-C}_4\text{F}_8/\text{CF}_4$, $c\text{-C}_4\text{F}_8/\text{CF}_4$, and SF_6/CF_4 . The familiar saturation (or "synergistic") characteristic⁶⁹ of SF_6/N_2 mixtures is practically absent. This result implies that SF_6/N_2 mixtures are superior to SF_6/CF_4 mixtures. With fluorocarbon gases, the characteristics of CF_4 mixtures are very close to those of fluorocarbon/ N_2 mixtures and their breakdown strengths are about the same, with no evident "synergism" in either.

Studies have also been made on the effects of surface roughness with these mixtures. Figures 34 through 37 present the breakdown data for SF_6/CF_4 , $c\text{-C}_4\text{F}_8/\text{CF}_4$, and $2\text{-C}_4\text{F}_8/\text{CF}_4$ mixtures on two 0.75-cm radius inner electrodes but each with a different degree of surface roughness.

Fig. 32. Breakdown voltages for three attaching gas/ CF_4 mixtures with negative polarity on the 0.75-cm radius inner electrode.

Fig. 33. Breakdown voltages for the three attaching gas/ CF_4 mixtures with positive polarity on the 0.75-cm radius inner electrode.

Fig. 34. Breakdown voltages for the attaching gas/ CF_4 mixtures with negative polarity on the 0.75-cm radius inner electrode. Inner electrode has 2 in. long center section with spiral grooves 0.004 in. deep.

Fig. 35. Breakdown voltages for the attaching gas/ CF_4 mixtures with positive polarity on the 0.75-cm radius inner electrode. Inner electrode has 2 in. long center section with spiral grooves 0.004 in. deep.

Fig. 36. Breakdown voltages for the attaching gas/ CF_4 mixtures with negative polarity on the 0.75-cm radius inner electrode. Inner electrode has 2 in. long center section with spiral grooves 0.02 in. deep.

Fig. 37. Breakdown voltages for the attaching gas/ CF_4 mixtures with positive polarity on the 0.75-cm radius inner electrode. Inner electrode has 2 in. long center section with spiral grooves 0.02 in. deep.

Again, the saturation characteristic seen with SF_6/N_2 mixtures is absent for SF_6/CF_4 , and the breakdown curves of the fluorocarbon/ CF_4 mixtures are straight lines. The breakdown strengths are reduced, depending on the degree of surface roughness. Figures 38 through 43 compare the data for these rough electrodes with the data for the same electrodes but with smooth surfaces. Figures 38 and 39 suggest that SF_6/CF_4 mixtures are almost insensitive to small surface roughness (but not so for pure SF_6) and for large surface roughness the least sensitivity to surface roughness can be obtained with a mixture of ~5% SF_6 and 95% CF_4 . For fluorocarbon/ CF_4 mixtures, a mixture of about the same ratio is least sensitive to surface roughness as shown in Fig. 40 through 43.

C. Cylindrical Geometry Breakdown Tests with 1,1,1- $\text{C}_2\text{F}_3\text{H}_3$ as the Moderator

The $\text{c-C}_4\text{F}_8/1,1,1\text{-C}_2\text{F}_3\text{H}_3$ mixtures have been studied with smooth electrodes of inner radii of 0.4, 0.75, and 1.4 cm. The breakdown data are presented in Fig. 44. All the breakdown curves are characterized by their saturation effects. This "synergism" suggests that $\text{c-C}_4\text{F}_8/1,1,1\text{-C}_2\text{F}_3\text{H}_3$ mixtures have higher breakdown strengths as compared with $\text{c-C}_4\text{F}_8/\text{N}_2$ mixtures and $\text{c-C}_4\text{F}_8/\text{CF}_4$ mixtures. The studies of 1,1,1- $\text{C}_2\text{F}_3\text{H}_3$ as a moderator with other attaching gases will be continued, since this is the first moderating gas we have found to show "synergism" with an attaching gas other than SF_6 (SF_6 shows "synergism" with N_2).

Fig. 38. Ratios of breakdown voltages for SF_6/CF_4 mixtures with negative rough (grooved) inner electrode (V_R) and with smooth electrodes (V_{SM}) of 0.75-cm radius, each with outer cylinder radius of 2 cm.

Fig. 39. Ratios of breakdown voltages for SF_6/CF_4 mixtures with positive rough (grooved) inner electrodes (V_R) and with smooth electrodes (V_{SM}) of 0.75-cm radius, each with outer cylinder radius of 2 cm.

Fig. 40. Ratios of breakdown voltages for $c\text{-C}_4\text{F}_8/\text{CF}_4$ mixtures with negative rough (grooved) inner electrodes (V_R) and with smooth electrodes (V_{SM}) of 0.75-cm radius, each with outer cylinder radius of 2 cm.

Fig. 41. Ratios of breakdown voltages for $c-C_4F_8/CF_4$ mixtures with positive rough (grooved) inner electrodes (V_R) and with smooth electrode (V_{SM}) of 0.75-cm radius, each with outer cylinder radius of 2 cm.

Fig. 42. Ratios of breakdown voltages for 2-C₄F₈/CF₄ mixtures with negative rough (grooved) inner electrodes (V_R) and with smooth electrode (V_{SM}) of 0.75-cm radius, each with outer cylinder radius of 2 cm.

Fig. 43. Ratios of breakdown voltages for 2-C₄F₈/CF₄ mixtures with positive rough (grooved) inner electrodes (V_R) and with smooth electrode (V_{SM}) of 0.75-cm radius, each with outer cylinder radius of 2 cm.

Fig. 44. Breakdown voltages in three cylindrical geometries for $c\text{-C}_4\text{F}_8/1,1,1\text{-C}_2\text{F}_3\text{H}_3$ mixtures with negative polarity on inner electrode.

D. Diverter Studies

An apparatus for studying the mechanisms for breakdown in triggered gaps has been assembled (see Sect. VIII). The triggered gap previously employed for diverting the energy from one of our breakdown apparatuses is being used. Some photographs of the air gap triggered breakdown using the Imacon 790 image converter camera have been taken to check the camera-diverter system.

Due to the uneven nature of the discharge in the main gap, it is difficult to take streak photographs of the discharge. However, optics have been ordered that will allow streak photography of the discharge.

Our plans are to perform a series of measurements of time-to-breakdown using only an oscilloscope so that the operating parameters of the gap are well documented before detailed photographic study of the gap is begun.

VII. LIQUID DIELECTRICS*

Validation of the experimental apparatus was carried out during this period. The purification system described in our last report¹⁸ has been thoroughly checked so that oxygen content of the liquid under test is less than one part per million. Initial data using n-hexane showed erratic behavior, but the addition of an electrostatic precipitator and the implementation of more refined cleaning techniques eliminated most of the problems. Photographs of the apparatus and test cell are shown in Figs. 45 and 46.

Further improvements in breakdown results were obtained by adding glass filters to remove small, solid particles of lint. Many investigators have reported⁷⁰ that the most pronounced effect on dielectric strength is the presence of impurities. Our data in Fig. 47 confirms this consensus in that the breakdown strength of n-hexane ($n\text{-C}_6\text{H}_{14}$) significantly improves as filters are added (average breakdown values change from 0.41 to 0.54 to 0.74 MV/cm). To further enhance the removal of particles, a 0.5 μ filter will be added in future experiments.

The breakdown voltage (0.74 MV/cm) for n-hexane filtered by 4 μ and 2 μ filters is in very close agreement with that obtained by Maksiejewski and Tropper⁷¹ under similar conditions (0.749 MV/cm). In all of the cases reported here, the applied voltage is gradually increased until breakdown occurs. Other investigators have reported⁷² dielectric strengths of twice these values when applying the voltage in a pulse form to eliminate

*This work was carried out jointly with J. G. Carter

ORNL PHOTO 5391-78

Fig. 45. Overall view of liquid breakdown test apparatus, showing purification apparatus, test cell (with corona ring on bottom), and shielded voltmeter.

ORNL PHOTO 1900-79

Fig. 46. Liquid breakdown test cell, showing spherical electrode gap through quartz window and micrometer gap adjustment.

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Fig. 47. Liquid breakdown voltages vs. gap between spherical electrodes.

the formation of bubbles within the test cell and to characterize the electrical performance of the pure liquid more closely. In our studies, we are including the susceptibility the liquid has for decomposition under stress and the subsequent formation of bubbles, which is the case in practical implementations in transformers and circuit breakers.

In view of our earlier findings on high dielectric strengths of gaseous perfluorocarbons we made some breakdown measurements on perfluoro-n-hexane ($n\text{-C}_6\text{F}_{14}$). The data in Fig. 47 show a slight improvement (0.54 to 0.59 MV/cm) over n-hexane measured after filtering. This improvement was expected since gas bubbles formed just prior to breakdown probably would retain the excellent fluorocarbon gas characteristics and inhibit breakdown.

Since $n\text{-C}_6\text{F}_{14}$ is expensive, measurements have not yet been obtained for the double filtering case. However, *mixtures* of $n\text{-C}_6\text{F}_{14}$ and n-hexane were tried out. It was observed that for an applied voltage of 10 kV or more the mixtures bubbled violently, turned cloudy and experienced breakdown shortly thereafter. Perhaps the high field associated with these voltages caused this turbulent behavior. The data in Fig. 47 show that the mixtures are less effective than either liquid alone (0.54 and 0.68 versus 0.74 or higher MV/cm) and that the greater the percentage of $n\text{-C}_6\text{F}_{14}$ the higher the breakdown (0.68 versus 0.54 MV/cm).

Additional data was obtained for n-heptane to validate further the experimental apparatus. These measurements show an improvement over n-hexane (0.74 to 0.81 MV/cm) just as Sharbaugh et al.⁷² found using the pulsed voltages (1.56 to 1.66 MV/cm).

These preliminary experiments have given us experience in testing liquids and have validated our experimental apparatus. It appears that

perfluoro-n-hexane alone has higher breakdown strength than n-hexane but that a mixture of the two is rather impractical. Additional experiments will be performed to confirm these preliminary findings and to investigate the behavior of liquid dielectrics under stress. Our focus will be on halocarbons.

VIII. APPARATUS

A. Quadrupole Mass Spectrometer

The quadrupole mass spectrometer purchased from Extranuclear Laboratories has been received. It is based on their SpectrEL mass spectrometer system. A photograph of the instrument is given in Fig. 48 and a diagram in Fig. 49. The high pressure spark ion source was designed and fabricated at our laboratory. Figure 50 is a photograph of the ion source, and Fig. 51 is a scale drawing of a section of the ion source.

Ions may be produced in two regions of the instrument, either in the high pressure spark source, or by an electron beam in the region between the aperture and the ion focusing lenses. The ion source and inlet chambers are separated by a removable pin-hole aperture. A 0.002-in. diam aperture allows a pressure of 350 torr in the ion source while still maintaining a pressure of 2×10^{-4} torr in the inlet chamber. This is made possible by the relatively high pumping speed (500 liters/sec) turbomolecular pump on the inlet chamber. An aperture of 0.0015 in. diam enables a pressure of 700 torr in the ion source for the same inlet chamber pressure. Ions produced by the spark between the two electrodes diffuse outward, and a fraction of these ions, along with a larger quantity of background gas diffuses through the aperture into the inlet chamber. The ions are focused by the ion lenses into the quadrupole mass analyzer. In addition, ions may be produced by the electron impact ionizer, allowing the detection of neutral species which are produced in the ion source.

Fig. 48. Photograph of the quadrupole mass spectrometer and its associated electronics.

Fig. 49. Diagram of quadrupole mass spectrometer. 1) Linear motion feedthrough. 2) Ion source chamber. 3) High voltage feedthroughs. 4) Electrode support insulator. 5) Centering insulator. 6) Electrode mounting rails. 7) Electrodes. 8) Pin-hole aperture. 9) Filament. 10) Ion focusing lenses. 11) Quadrupole mass filter. 12) Faraday plate. 13) Channeltron electron multiplier. 14) Inlet chamber. 15) 500 μ /sec turbo pump. 16) Detector chamber. 17) 100 μ /sec turbo pump.

Fig. 50. Photograph of the high pressure spark ion source components.

Fig. 51. Diagram of the pressure spark ion source. 1) Linear motion feedthrough. 2) Ion source chamber. 3) High voltage feedthroughs. 4) Electrode support insulator. 5) Centering insulator. 6) Electrode mounting rails. 7) Electrodes. 8) Pin-hole aperture. 9) Line-to-vacuum pump. 10) Line-to-pressure gauge. 11) Line-to-gas supply.

The quadrupole is 20 cm long, with a pole diameter of 9.5 mm, covering the mass range from 3 to 1000 amu (atomic mass units) with better than unit mass resolution over the entire range. The quadrupole can be set to pass a single mass, or it can be scanned at rates up to 1000 amu/sec.

The ions can be detected with the Faraday plate and an electrometer amplifier, or they can be detected with the channel electron multiplier and the associated pulse counting electronics.

The normal operating pressure in the inlet chamber is 1×10^{-4} torr, and the normal pressure in the detector chamber is 1×10^{-6} torr. The turbomolecular pumps are an advantage because of their fast response and because they do not produce a hydrocarbon fragment background as do oil diffusion pumps.

The quadrupole system has several advantages over other types of mass filters for our purposes. Higher operating pressures can be tolerated since small angle collisions between the ions and the background gas molecules do not affect the resolution of the quadrupole because of the wide acceptance angle and the insensitivity to differences in ion velocity. High voltage is not required for ion extraction or transmission. The trade-off between resolution and intensity can easily be optimized for a given application by simply varying an electronic control. Masses may be scanned very rapidly without changing the ion-optical properties of the system. The physical size of the instrument is small and compact. Finally, the quadrupole is a true mass-to-charge ratio filter, unlike a magnetic sector, which is only a momentum filter.

The ion source can be operated at pressures from vacuum to slightly over 1 atm, depending on the size of the "pin-hole" sampling aperture

being used. The source chamber is fabricated from stainless steel, as are all the parts except for the insulators, which are made of Lavite, and the high voltage feedthroughs and electrodes, which can be made of several different materials (e.g., tungsten, tantalum, molybdenum, copper, or aluminum). The electrode gap is adjustable, as is the distance between the electrodes and the aperture. In normal operation, the source is baked at 100°C to eliminate as much as possible traces of water vapor.

Because of the product particle path length and the chamber pressure, ions and neutrals will undergo many collisions before they diffuse to the aperture. Therefore, the ions and neutrals that do reach the aperture should be of thermal energy. These conditions are therefore much closer to the actual conditions encountered in the commercial applications of dielectric gases than would be the conditions in a conventional mass spectrometer. Furthermore, it is possible to detect species that are too reactive to be seen by other analytical techniques due to reaction with the walls of the containers used.

B. Gas Chromatograph

A model Sigma 3 gas chromatograph has been ordered from the Perkin-Elmer Corporation. This is a dual channel, microprocessor-controlled, temperature-programmed instrument. It is equipped with dual digital carrier gas flow controllers, dual heated 1/8 in. injectors, and dual thermal conductivity detectors. Flame ionization and electron capture detectors may be added in the future, if desired. The instrument is also equipped with a gas sampling valve to make the injection of the gaseous

samples more convenient. Columns have been purchased packed with silica gel, molecular sieve 5A, Porapak Q, 0.1% SP-1000 on Carbopack C, and Duropak n-octane on Porasil C. These packings were chosen to enable us to optimize the separation of the various decomposition products.

Provision is being made to interface this gas chromatograph with the quadrupole mass spectrometer to aid in the unambiguous identification of the various effluent fractions.

The gas chromatograph will provide us with self sufficiency toward the analysis of final decomposition products of sparked and stressed dielectric gases.

C. High Pressure Chamber for Applied Test Apparatus

The new higher pressure chamber was completed, installed, checked, and used this period. It allows applied testing up to 10 atm total pressure, as compared to only 1 atm with the chamber previously used. The new chamber is seen installed in Fig. 52. It has an inside diameter of 10 in. and a length of approximately 30 in., with several ports--including a Delta Ray high voltage cable feedthrough and an ultraviolet transmitting window. Retained from the previous chamber were 30 kV ground lead feedthrough, small auxiliary chamber for freezing out gases, pumps, and pressure gauges. A 100 kV ceramic feedthrough has been purchased for a side port for future studies of triggered breakdown.

The high pressure integrity of the new chamber was tested by ORNL engineers before installation. We found the vacuum base pressure to be $\sim 5 \times 10^{-6}$ torr, and the vacuum with the Delta Ray feedthrough to be $\sim 5 \times 10^{-5}$ torr. Following pump-down to these vacuum levels we measured an outgassing rate of $\sim 25 \mu/\text{hr}$.

Fig. 52. Applied studies breakdown apparatus, seen through door of shielding cage, with new chamber and new power supply installed.

The new delta Ray 300 kV DC power supply was installed in the applied studies apparatus at the same time the chamber was. The HV SF₆ power supply tank can be partially seen in Fig. 52 with the cable arched over and into the end of the new chamber. The new supply operates satisfactorily with the automatic control system that we built earlier.

D. Small Breakdown Test Chamber

A small chamber ($\sim 350 \text{ cm}^3$ volume) was designed and fabricated to perform preliminary breakdown studies using very small quantities of gas. This test chamber is a standard stainless steel cross with 2.75 in. OD ConFlat flanges (Varian Associates #952-5050). The high voltage electrode is a 3/8 in. stainless steel sphere attached to the end of a 30 KV peak electrical feedthrough (Ceramaseal #808C6529-3). The ground electrode is a 3/8 in. stainless steel sphere which is attached to a linear motion feedthrough (Varian Associates #954-5150). To insure precise electrode adjustment, a 0-25 mm micrometer was adapted to the linear motion feedthrough. Both feedthroughs are mounted on opposing ports of the cross. A UV grade sapphire viewing port (Varian Associates #954-5035) is attached to a port on the cross, to permit viewing the chamber interior and irradiation of the electrodes with UV light. The port opposite the viewing port is used as a gas inlet and exhaust. This test chamber is enclosed in a Lexan box (6 in. x 8 in. x 16 in.), which is vented by way of an exhaust fan to the building exhaust system. A mirror manufactured by Melles Griot reflects UV light into the chamber through the viewing port.

E. Long-Term Stress Cells

Eleven chambers were assembled for use in long-term stress experiments. The cells are 10-cm long stainless steel cylinders with an internal volume of $\sim 140 \text{ cm}^3$. Two spherical electrodes, 2 cm in diameter, were mounted on support rods attached to a 2 3/4 in. Varian ConFlat flange via two ceramic vacuum feed-throughs. At the opposite end of the chamber a gas inlet line and valve were attached to another 2 3/4 in. Varian ConFlat flange. All cells were vacuum tested to pressures of $\sim 1 \times 10^{-6}$ torr.

F. Diverter; Impulse

The diverter apparatus consists of the diverter gap, an optical isolator circuit to trigger the spark gap while electrically isolating the operator from the gap, an image converter camera to photograph the development of the spark with sub-microsecond exposure times, and various electronic circuitry and power supplies.

The new impulse generator is scheduled to be shipped by the manufacturer in late May.

IX. SECOND INTERNATIONAL SYMPOSIUM ON GASEOUS DIELECTRICS

In March 1978, we hosted the first International Symposium on Gaseous Dielectrics sponsored by the U.S. Department of Energy, Oak Ridge National Laboratory, and the Electric Power Research Institute (EPRI) in cooperation with the Institute of Electrical and Electronics Engineers (IEEE)--and brought together leading individuals from universities, research laboratories, industrial centers, and funding agencies from throughout the world. Since a strong interest was expressed for continuation of this interaction, a second meeting has been planned. The purpose of the meeting--to be held March 9-13, 1980, at the Hyatt Regency Hotel in Knoxville, Tennessee--is identical to the first, namely, to provide a forum for review and discussion of the progress and the problems of current interest in gaseous dielectrics and their use, especially as insulators in high-voltage transmission lines and substations. It will be sponsored by DOE and ORNL, in cooperation with EPRI and IEEE.

With the assistance of an international organizing committee, the advance program was formulated and mailed in February 1979 to about 500 individuals. The number of attendees will be limited to a maximum of 150. Abstracts of papers are due by August 1, 1979. Potential participants will be reminded of this deadline through a postcard to be mailed out early in June 1979.

X. PUBLICATIONS AND CONTACTS

A. Publications

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12. K. Siomos, G. Kourouklis, L. G. Christophorou, and J. G. Carter, "Photoionization of Fluorescent Organic Molecules in Liquid Media," *Int. J. Rad. Phys. Chem.* (submitted)
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B. Contacts

In this period, we have had technical discussions with many individuals, including Zane Egan (Chemical Technology, Oak Ridge National Laboratory); Dave Bodwell, Steve Fehl, and Dick Jesser (Perkin-Elmer); John Crane (Lawrence Livermore Laboratory); Ed Thomas, Mel Siegel, and John Zamaria (Extranuclear Laboratories); Martin Mastroianni (Allied Chemical); and Roy Wootton (Westinghouse).

In this period, we have been visited among others by Richard J. Van Brunt, Martin Misakian, Robert E. Hebner (National Bureau of Standards); Bruce Best (Air Products); G. Freeman (University of Alberta); Steven Rice (University of Toronto); Arthur Kwong, Abdol Fatheddin, Cuong Nguyen, Torsak Inyai, Fred Carden, Jr. (Electrical Engineering, University of Tennessee); Eric Larsen (W. A. Brown Instruments); and Timothy Kaiser (Tektronix). A seminar and tour were given to a group from the Electric Power Research Institute, *viz.* S. J. Dale (Westinghouse), Alan Cookson (Westinghouse), George Adams (Niagara Mohawk Power Corp.), K. Bechet (Boston Edison), J. Duston (Arizona Public Service), R. Luther (Northeast Utilities), R. Mann (Southern California Edison), J. Pachot (Bonneville Power Administration), J. Therkell (Bureau of Reclamation), C. Aikens (Tennessee Valley Authority), and J. Shimshock (Electric Power Research Institute).

Dr. Harry W. Ellis will join our group for six weeks this summer through an ORAU (Oak Ridge Associated Universities) grant to work with Drs. I. Sauers and L. Frees on the atmospheric pressure quadrupole mass

spectrometer in the environmental effects program. Dr. Ellis is presently a professor of physics at Eckerd College in St. Petersburg, Florida. He has had considerable experience with quadrupole mass spectrometers and in the physics of ion-molecule reactions. His support will be entirely through ORAU.

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APPENDIX A

Electron Attachment to Perfluorocarbon Compounds.

I. $c\text{-C}_4\text{F}_6$, $2\text{-C}_4\text{F}_6$, $1,3\text{-C}_4\text{F}_6$, $c\text{-C}_4\text{F}_8$ and $2\text{-C}_4\text{F}_8$

A. A. Christodoulides, L. G. Christophorou, R. Y. Pai, and C. M. Tung

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Electron attachment to perfluorocarbon compounds. I. $c\text{-C}_4\text{F}_6$, $2\text{-C}_4\text{F}_6$, $1,3\text{-C}_4\text{F}_6$, $c\text{-C}_4\text{F}_8$ and $2\text{-C}_4\text{F}_8$ ^{a)}

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Electron attachment rates α_w , as a function of the pressure-reduced electric field E/P_{00} and mean electron energy $\langle \epsilon \rangle$ have been measured for trace amounts ($< 10^{-3}$ Torr) each of $c\text{-C}_4\text{F}_6$ (perfluorocyclobutene), $2\text{-C}_4\text{F}_6$ (perfluoro-2-butyne), $1,3\text{-C}_4\text{F}_6$ (perfluoro-1,3-butadiene), $c\text{-C}_4\text{F}_8$ (perfluorocyclobutane), and $2\text{-C}_4\text{F}_8$ (perfluoro-2-butene) in mixtures with N_2 (pressures 500–2000 Torr) and Ar (pressures 500–1500 Torr) at $T = 298^\circ\text{K}$. The thermal attachment rates for these molecules were found to be 4.89×10^9 , 1.77×10^9 , 4.26×10^9 , 4.05×10^9 , and $1.56 \times 10^9 \text{ sec}^{-1} \text{ Torr}^{-1}$, respectively. From the $\alpha_w(\langle \epsilon \rangle)$ data, the attachment cross sections $\sigma_a(\epsilon)$ as a function of electron energy ϵ have been determined using the swarm-unfolding technique and are reported. For all five perfluorocarbon molecules, $\sigma_a(\epsilon)$ are very large. They exhibit three distinct negative ion resonances with maxima at: ~ 0.0 , 0.19 , and 0.80 eV for $2\text{-C}_4\text{F}_6$; ~ 0.0 , 0.17 , and 1.04 eV for $1,3\text{-C}_4\text{F}_6$; ~ 0.0 , 0.22 , and 0.48 eV for $c\text{-C}_4\text{F}_8$; and ~ 0.0 , 0.18 , and 0.59 eV for $2\text{-C}_4\text{F}_8$. For $c\text{-C}_4\text{F}_6$, only a shoulder with a possible maximum at $\sim 0.14 \text{ eV}$ was observed, in addition to the maxima at ~ 0.0 and 0.71 eV . Although the positions of the maxima in $\sigma_a(\epsilon)$ vary only slightly among these compounds, the magnitude of $\sigma_a(\epsilon)$ depends strongly on structure.

I. INTRODUCTION

Electron attachment studies are of fundamental importance in the development of a basic understanding of molecules and their interactions with slow electrons. They are also of a considerable practical interest. For example, perfluorinated hydrocarbons have a potential use as high voltage gaseous insulators (see, for example, Refs. 1 to 4 for recent work). The high breakdown strength of these gases is principally ascribed to their high electron attachment cross sections at low energies, as is discussed in this and the following paper (Part II). However, there is little quantitative information in the literature concerning their electron attachment properties in the energy range from thermal to $\sim 3 \text{ eV}$.

In this paper (Part I), we report on and discuss the capture of slow ($\leq 3 \text{ eV}$) electrons by the perfluorocarbons $c\text{-C}_4\text{F}_6$, $2\text{-C}_4\text{F}_6$, $1,3\text{-C}_4\text{F}_6$, $c\text{-C}_4\text{F}_8$, and $2\text{-C}_4\text{F}_8$. The determination of the magnitude of the thermal electron attachment rate, the magnitude and energy dependence of the electron attachment rate and cross section, the position of the negative ion resonance states below $\sim 1.4 \text{ eV}$, the possible reaction mechanisms for formation and dissociation of the parent negative ions, and the effect of molecular structure on the electron capture processes at low energies are the principal concerns of this work.

II. EXPERIMENTAL SECTION

The electron-swarm method employed in the present study has been described in detail earlier.^{5–7} All mea-

surements were performed at room temperature ($T = 298^\circ\text{K}$). The carrier gases N_2 and Ar were used at pressures ranging from 500 to 2000 torr and from 500 to 1500 torr, respectively, and were of the highest purity available. The pressure ranges of the perfluorocarbons (C_4F_6 or PFC) investigated are given in Table I. All compounds were provided by Columbia Organic Chemicals Company with a guaranteed purity of $> 97\%$. The PFC molecules attach electrons very strongly (see Sec. IV) and for this reason minute amounts of these compounds had to be used in the experiments. In order to increase the accuracy of the pressure measurements, an expansion procedure was employed whereby the attaching gas was introduced into a small volume at higher pressure and then expanded into the experimental chamber. The ratio of the volume of the experimental (main) chamber to the auxiliary chamber was 520:1. Bake-out facilities were provided to remove possible adsorbed gases on the walls of the chamber and the gas manifold. A vacuum of $\sim 3 \times 10^{-8}$ torr was usually reached in the experimental chamber prior to the introduction of the PFC gases.

The possible errors in our measurements are both systematic and random.

Systematic errors. There are three sources of systematic errors: the electrode separation distance (electron drift distance), the voltage applied to the electrodes, and the presence of impurities. The electrode separation can be measured to better than $\pm 0.5\%$. The applied voltage is measured by a calibrated digital voltmeter to $\pm 0.01\%$. Impurities due to outgassing are negligible, since we routinely pumped the vacuum system to 10^{-8} torr before introduction of the gas in the experimental chamber.

The major source of systematic uncertainty is due to any impurities in the sample, as supplied by the manufacturer. All compounds were better than 97% pure. The error introduced by impurities is usually large when the studied compound attaches electrons

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TABLE I. Nomenclature, structural formulas, pressure ranges used, and boiling and freezing points for $c\text{-C}_4\text{F}_8$, $2\text{-C}_4\text{F}_8$, $1,3\text{-C}_4\text{F}_6$, $c\text{-C}_4\text{F}_6$, and $2\text{-C}_4\text{F}_6$.

Perfluorocarbon	Molecular formula	Structural formula	$P_{C_2F_6}$ in N_2 ^a (10^{-3} torr)	$P_{C_2F_6}$ in Ar ^b (10^{-3} torr)	Boiling point (°C)	Freezing point (°C)
Perfluorocyclobutene	$c\text{-C}_4\text{F}_6$		(15) ^c 4.3–88.4	(9) 42.7–146.1	0 ^d 1.13 ^f 3 ^e	–60 ^e –60.4 ^f –61 ^d
Perfluoro-2-butyne	$2\text{-C}_4\text{F}_6$		(11) 6.0–12.0	(4) 7.6–9.5	–24 to –23 ^e –24.6 ^e –25 ^b	–117.4 ^e
Perfluoro-1,3-butadiene	$1,3\text{-C}_4\text{F}_6$		(8) 6.7–9.6	(5) 9.2–14.0	6.0 ^d 6.0 ^e 6.6 ^f	–132 ^d –132.4 ^e
Perfluorocyclobutane	$c\text{-C}_4\text{F}_8$		(8) 8.0–16.0	(4) 8.0–1	–5 ^f –6 ^f	–38.7 ^e 40 ^f –41.0 ^f
Perfluoro-2-butene	$2\text{-C}_4\text{F}_8$		(11) 8.0–12.0	(8) 8.0–14.0	0.4 to 3.0 ^f	–129 to –139 ^f

^aThe pressures of N_2 employed are 500, 1000, 1500, and 2000 torr.^bThe pressures of Ar employed are 500, 1000, and 1500 torr.^cThe numbers in parentheses give the number of independent runs made in N_2 or Ar.^dJ. H. Simons and T. J. Brice, *Fluorine Chemistry*, edited by J. H. Simons (Academic, New York, 1954), Vol. II, Chap. 6, p. 405.^eHandbook of Chemistry and Physics (Chemical Rubber, Cleveland, 1974–1975), 55th Edition, p. C-75.^fW. H. Pearson, *Fluorine Chemistry*, edited by J. H. Simons (Academic, New York, 1950), Vol. I, Chap. 14, p. 500.^gT. J. Brice, *Fluorine Chemistry*, edited by J. H. Simons (Academic, New York, 1950), Vol. I, Chap. 13, p. 452.^hE. R. Larsen, *Fluorine Chem. Rev.* 3, 1 (1969).ⁱH. G. Bryce, *Fluorine Chemistry*, edited by J. H. Simons (Academic, New York, 1964), Vol. V, Chap. 4, p. 347.

weakly and the impurities strongly. The perfluorocarbons investigated in this work, however, have very large electron attachment rates, over a wide electron energy range. Thus, it is anticipated that any error due to impurities is $\leq 3\%$.

Random errors. Errors in measurements of the total and especially partial pressures, uncertainties in extrapolation of the peak pulse height at zero time⁷ (initial time of introduction of attaching gas in the experimental chamber) for all E/P values used, and recording the peak of the pulse height distribution are sources of random error which are reflected in the variation of the measured attachment rates from run to run.

The attachment rates that we measure fall within an envelope of 10% of the average values given in Tables II and III (see Sec. IV. B). This spread is primarily due to uncertainties in the pressure measurement of PFC. It is emphasized that the random contribution of error does not affect the relative attachment cross sections that we unfold (see Sec. III. B). Unfolding the $\alpha w(\epsilon)$ functions from a single run gives the same relative cross section as the unfolding of an average set of αw values obtained from many runs.

III. BASIS OF MEASUREMENTS AND CALCULATIONS

A. The electron energy distribution function $f(\epsilon, E/P)$

In the electron swarm method, the electron attachment rate αw (α is the electron attachment coefficient in $\text{cm}^{-1} \text{ torr}^{-1}$ and w is the electron drift velocity in cm sec^{-1}) for a gas is measured as a function of the pressure-reduced electric field E/P (in units of $\text{V cm}^{-1} \text{ torr}^{-1}$) at constant temperature T . For every value of E/P , the distribution of electron energies $f(\epsilon, E/P)$ in the electron swarm depends strongly on the gas under study. The $f(\epsilon, E/P)$ are unknown for the PFC's investigated. To overcome this difficulty, our experiments were performed on binary gas mixtures, where the perfluorocarbon under study was mixed with the nonelectron attaching gas N_2 or Ar for which $f(\epsilon, E/P)$ are known^{5,7,8} over a suitable range of E/P values. Knowledge of $f(\epsilon, E/P)$ or $f(\epsilon, \langle \epsilon \rangle)$, where $\langle \epsilon \rangle$ is the mean electron energy, is necessary for a meaningful physical analysis of the raw experimental electron attachment data (see Sec. IV. C).

The compounds under investigation were mixed in very small proportions with the carrier gases (see Table I). This ensured that $f(\epsilon, E/P)$ in the mixture

TABLE II. Electron attachment rates for $c\text{-C}_4\text{F}_8$, $2\text{-C}_4\text{F}_8$, $1,3\text{-C}_4\text{F}_8$, $c\text{-C}_4\text{F}_8$, and $2\text{-C}_4\text{F}_8$ in N_2 .

E/P_{100} (V cm ⁻¹ torr ⁻¹)	$\langle \epsilon \rangle$ (eV)	$\alpha\omega$ in N_2 ($10^8 \text{ sec}^{-1} \text{ torr}^{-1}$)					$(\alpha\omega)_{\text{max}}^a$ ($10^8 \text{ sec}^{-1} \text{ torr}^{-1}$)
		$c\text{-C}_4\text{F}_8$	$2\text{-C}_4\text{F}_8$	$1,3\text{-C}_4\text{F}_8$	$c\text{-C}_4\text{F}_8$	$2\text{-C}_4\text{F}_8$	
0.02	0.046	4.20	1.69	3.85	0.45	1.48	13.25
0.03	0.054	3.73	1.60	3.55	0.48	1.40	12.55
0.04	0.064	3.30	1.53	3.28	0.54	1.34	11.44
0.05	0.075	2.98	1.49	3.10	0.61	1.30	10.60
0.06	0.087	2.68	1.43	2.93	0.67	1.25	9.70
0.07	0.099	2.45	1.40	2.79	0.76	1.21	9.05
0.10	0.131	1.97	1.34	2.53	0.93	1.17	7.85
0.15	0.181	1.47	1.29	2.20	1.14	1.10	6.60
0.20	0.230	1.14	1.27	1.92	1.25	1.03	5.85
0.25	0.285	0.94	1.28	1.70	1.31	0.98	5.30
0.35	0.376	0.67	1.33	1.35	1.31	0.89	4.60
0.50	0.490	0.46	1.36	1.03	1.20	0.77	3.97
0.60	0.550	0.40	1.38	0.91	1.13	0.73	3.72
0.80	0.646	0.30	1.38	0.75	1.01	0.64	3.40
1.00	0.715	0.26	1.33	0.68	0.91	0.59	3.20
1.20	0.764	0.23	1.27	0.62	0.84	0.54	3.08
1.40	0.803	0.20	1.22	0.57	0.77	0.50	3.00
1.70	0.846	0.17	1.15	0.52	0.71	0.46	2.93

^aThe values of $(\alpha\omega)_{\text{max}}$ were obtained using Eq. (9) and the $f_{N_2}(\epsilon, \langle \epsilon \rangle)$ functions for N_2 (see Sec. III.D).

remained basically unchanged, characteristic of the carrier gas alone.

B. The electron attachment cross section $\sigma_a(\epsilon)$

The rate $\alpha\omega(E/P)$ of electron attachment to a molecule is related to the electron attachment cross section $\sigma_a(\epsilon)$ (in units of cm^2) and $f(\epsilon, E/P)$ by

$$\alpha\omega(E/P) = N_0 \left(\frac{2}{\pi} \right)^{1/2} \int_0^\infty \epsilon^{1/2} \sigma_a(\epsilon) f(\epsilon, E/P) d\epsilon. \quad (1)$$

In Eq. (1), $N_0 (= 3.241 \times 10^{16})$ is the number of electron attaching molecules per cm^3 per torr at 298°K, and m is the electron mass.

Two techniques have been developed for the determination of $\sigma_a(\epsilon)$ from electron-swarm experiments via Eq. (1): the swarm-beam⁹ and the swarm unfolding¹⁰

techniques. In the former, $\sigma_a(\epsilon)$ is obtained through a combination of the measured $\alpha\omega(\langle \epsilon \rangle)$ data from electron-swarm experiments with the measured negative ion yield $I(\epsilon)$ data from electron-beam experiments. In the latter, which is the one employed in the present study, $\sigma_a(\epsilon)$ is determined from the $\alpha\omega(\langle \epsilon \rangle)$ data alone and this can be done virtually at any gas density for which $f(\epsilon, E/P)$ is known and $\alpha\omega(\langle \epsilon \rangle)$ has been measured over a wide and convenient range of E/P . The rate $\alpha\omega$ is a quantity which is averaged over $f(\epsilon, E/P)$. Hence, we may write

$$\alpha\omega(\langle \epsilon \rangle) = \int_0^\infty \alpha\omega(\epsilon) f(\epsilon, \langle \epsilon \rangle) d\epsilon, \quad (2)$$

where $\alpha\omega(\langle \epsilon \rangle)$ is the experimentally measured value of $\alpha\omega$ at the mean electron energy $\langle \epsilon \rangle$, (i.e., at the j th value of E/P), $f(\epsilon, \langle \epsilon \rangle)$ is the electron energy distribu-

TABLE III. Electron attachment rates for $c\text{-C}_4\text{F}_8$, $2\text{-C}_4\text{F}_8$, $1,3\text{-C}_4\text{F}_8$, $c\text{-C}_4\text{F}_8$, and $2\text{-C}_4\text{F}_8$ in Ar.

E/P_{100} (V cm ⁻¹ torr ⁻¹)	$\langle \epsilon \rangle$ (eV)	$\alpha\omega$ in Ar ($10^8 \text{ sec}^{-1} \text{ torr}^{-1}$)					$(\alpha\omega)_{\text{max}}^a$ ($10^8 \text{ sec}^{-1} \text{ torr}^{-1}$)
		$c\text{-C}_4\text{F}_8$	$2\text{-C}_4\text{F}_8$	$1,3\text{-C}_4\text{F}_8$	$c\text{-C}_4\text{F}_8$	$2\text{-C}_4\text{F}_8$	
0.010	0.498		12.39	9.57	11.32	7.67	38.90
0.015	0.570		13.39	8.33	10.47	7.27	36.33
0.02	0.641	2.68	13.61	7.50	9.63	6.86	33.92
0.03	0.752	2.22	13.29	6.67	8.20	5.97	31.32
0.04	0.848	1.88	12.22	5.78	7.03	5.16	29.00
0.05	0.935	1.62	11.08	5.23	6.08	4.52	28.14
0.06	1.012	1.41	9.99	4.70	5.30	4.04	27.04
0.10	1.285	0.97	7.26	3.47	3.77	2.80	23.76
0.15	1.559	0.71	5.44	2.63	2.67	2.08	21.12
0.20	1.797	0.58	4.40	2.20	2.08	1.66	18.70
0.25	2.008	0.48	3.77	1.90	1.76	1.38	16.65
0.30	2.197	0.44	3.32	1.70	1.53	1.22	14.98
0.40	2.526	0.36	2.75	1.40	1.24	0.98	12.51
0.50	2.808	0.30	2.26	1.20	1.04	0.82	10.81

^aThe values of $(\alpha\omega)_{\text{max}}$ were obtained using Eq. (9) and the $f_{\text{Ar}}(\epsilon, \langle \epsilon \rangle)$ functions for Ar (see Sec. III.D).

tion function that corresponds to $\langle \epsilon \rangle$, and $\alpha w(\epsilon)$ is the value of the monoenergetic attachment rate at the electron energy ϵ (i.e., the value of the attachment rate that would be measured, if all the electrons in the swarm had the same energy ϵ). Equation (2) forms the basis of the swarm unfolding technique. Christophorou *et al.*¹⁰ have described an iterative procedure which allows $\alpha w(\epsilon)$ to be unfolded from the measured $\alpha w(\langle \epsilon \rangle)$ using the corresponding known $f(\epsilon, \langle \epsilon \rangle)$ functions. Once $\alpha w(\epsilon)$ is determined, $\sigma_a(\epsilon)$ is obtained from

$$\sigma_a(\epsilon) = \frac{\alpha w(\epsilon)}{N_0(2/m)^{1/2} \epsilon^{1/2}} = 5.225 \times 10^{-25} \frac{\alpha w(\epsilon)}{\epsilon^{1/2}}, \quad T = 298^\circ \text{K}. \quad (3)$$

In Eq. (3), the units of $\sigma_a(\epsilon)$ are in cm^2 and the units of ϵ in eV.

The number of iterations required for convergence of the $\alpha w(\epsilon)$ functions is usually ~ 1000 , although in the present study we have always performed ~ 3000 iterations. The extent to which the experimental $[\alpha w(\langle \epsilon \rangle)]_{\text{exptl.}}$ and the calculated $[\alpha w(\langle \epsilon \rangle)]_{\text{calc.}}$ values agree can be assessed from the value of the ratio R , defined as

$$R = \frac{\sum_i \{[\alpha w(\langle \epsilon \rangle)]_{\text{exptl.}} - [\alpha w(\langle \epsilon \rangle)]_{\text{calc.}}\}^2}{\sum_i [\alpha w(\langle \epsilon \rangle)]_{\text{exptl.}}^2}. \quad (4)$$

The lower the value of R , the better the overall agreement between the experimental and the calculated $\alpha w(\langle \epsilon \rangle)$ values, and hence the closer is the final function $\alpha w(\epsilon)$ to the true monoenergetic attachment rate. In all cases considered in this paper, R was $\sim 10^{-6}$.

C. The maximum electron attachment cross section $\sigma_{a, \text{max}} (= \pi \lambda^2)$

The integral electron scattering or reaction cross section σ_{tot} for a spherically symmetric potential field is¹¹

$$\sigma_{\text{tot}} = \frac{\pi}{k^2} \sum_l (2l+1) |S_{\text{tot}} - \delta_{\text{tot}}|^2, \quad (5)$$

where $k = 2\pi/\lambda = 1/\lambda$ is the wave number for the incoming wave (λ is the de Broglie wavelength of the electron), $l(=0, 1, 2, 3, \dots)$ is the angular momentum quantum number, S_{tot} is the scattering matrix for the initial state a and the final state b , δ_{tot} is a delta function of the energy of these states, and the reduced mass of the system was taken equal to the electron mass.

The sum of all reaction cross sections over all possible final channels $b \neq a$ (i.e., the total reaction cross section σ_r) is¹¹

$$\sigma_r = \frac{\pi}{k^2} \sum_{l=0}^{\infty} \sum_{b \neq a} (2l+1) |S_{ba}|^2 = \frac{\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) (1 - |S_{aa}|)^2. \quad (6)$$

S_{aa} expresses the matrix elements when only elastic scattering takes place.

The maximum value $(\sigma_r)_{\text{max}, l}$ of the partial reaction cross section for given l is obtained from Eq. (6):

$$(\sigma_r)_{\text{max}, l} = \frac{\pi}{k^2} (2l+1). \quad (7)$$

For a slow electron, the effective range of electron-molecule interaction is small compared with the electron de Broglie wavelength, and it can be assumed that only s waves ($l=0$) participate in the scattering. Thus, from Eq. (7), we have

$$\sigma_{a, \text{max}} = (\sigma_r)_{\text{max}, l=0} = \frac{\pi}{k^2} = \pi \lambda^2 = \frac{1.197 \times 10^{-15}}{\epsilon (\text{in eV})} \text{cm}^2. \quad (8)$$

In low-energy electron-swarm experiments, this can be considered to be the maximum (s -wave) electron capture cross section. Experimental $\sigma_a(\epsilon)$ are compared in Sec. IV.D with $\sigma_{a, \text{max}}$ at various values of the incident electron energy ϵ . It is apparent from these results that the measured $\sigma_a(\epsilon)$ are large, often $\geq 50\%$ of $\pi \lambda^2$ (see Figs. 8 and 9).

D. The maximum electron attachment rate $[\alpha w(\langle \epsilon \rangle)]_{\text{max}}$

To make a more direct comparison of the theoretical maximum (s -wave) electron capture rate with the experimental results, we determined through Eqs. (1) and (8) the maximum electron attachment rate as a function of $\langle \epsilon \rangle$, viz.,

$$\begin{aligned} [\alpha w(\langle \epsilon \rangle)]_{\text{max}} &= N_0 \left(\frac{2}{m} \right)^{1/2} \left(\frac{\pi \hbar^2}{2m} \right) \int_0^\infty \epsilon^{-1/2} f(\epsilon, \langle \epsilon \rangle) d\epsilon \\ &= 2.301 \times 10^9 \int_0^\infty \epsilon^{-1/2} f(\epsilon, \langle \epsilon \rangle) d\epsilon \quad (\text{sec}^{-1} \text{torr}^{-1}), \end{aligned} \quad (9)$$

where N_0 is the gas number density at $T = 298^\circ \text{K}$.

In the present work, the known^{5,7,8} $f(\epsilon, \langle \epsilon \rangle)$ functions for N_2 and Ar were used in the energy range of interest. A plot of $[\alpha w(\langle \epsilon \rangle)]_{\text{max}}$ as a function of $\langle \epsilon \rangle$ would lie above the experimentally measured $\alpha w(\langle \epsilon \rangle)$ values. The values for $[\alpha w(\langle \epsilon \rangle)]_{\text{max}}$ for N_2 and Ar are listed in Tables II and III, respectively (see Sec. IV.C).

E. The thermal electron attachment rate $(\alpha w)_{\text{ther}}$

The thermal value of the electron attachment rate for a molecule is an important parameter that many workers tried to obtain using a variety of experimental techniques (see Sec. V.D). For example, it is this parameter which is often used^{12,13} in comparisons of gaseous- and liquid-phase data on electron attachment. For many molecules, however, this quantity is uncertain due mainly to impurities, pressure dependencies, and nonthermal conditions for the electrons. As a rule,^{12,14} two or more electron attachment resonances exist below ~ 1 eV, often within a few tenths of 1 eV of thermal energy, which further complicates such determinations.

The thermal electron attachment rate can be determined in electron-swarm studies by (i) direct measurement at $E/P = 0$, which is practically not possible, and (ii) indirectly from αw vs E/P plots by extrapolation of the lower E/P attachment rate data to $E/P = 0$.

A third method for determining $(\alpha w)_{\text{ther}}$ has been suggested.¹² The monoenergetic attachment rate $\alpha w(\epsilon)$, as determined from the experimental $\alpha w(\langle \epsilon \rangle)$ data (see Sec. III.B) was used to obtain $(\alpha w)_{\text{ther}}$, viz.,

$$(\alpha w)_{\text{ther}} = \int_0^\infty \alpha w(\epsilon) f_{\text{th}}(\epsilon) d\epsilon, \quad (10)$$

where $f_M(\epsilon) = N_0 [2/\pi^{1/2} (kT)^{3/2}] e^{1/2} e^{-\epsilon/kT}$ is the Maxwellian electron energy distribution function at $T = 298^\circ\text{K}$. The determination of $(\alpha w)_{\text{thr}}$ in this way constitutes an accurate and convenient method, since measurement of αw for truly thermal electrons is rather difficult to make directly and accurately.

F. The energy integrated electron attachment cross section $\int_0^\infty \sigma_a(\epsilon) d\epsilon$

There are certain basic and applied areas, such as the field of gaseous dielectrics, where electron capture processes are of great importance (see Part II). In these cases, a comparison of the electron attaching efficiencies of molecules in a particular energy range in relation to each other and to $\sigma_{a,\text{max}}$ are most useful quantities. We thus introduce the ratio

$$R_{\epsilon_1}^{\epsilon_2} = \left[\frac{\int_{\epsilon_1}^{\epsilon_2} \sigma_a(\epsilon) d\epsilon}{\int_{\epsilon_1}^{\epsilon_2} \pi \kappa^2 d\epsilon} \right] \quad (11)$$

of the integrated cross sections for capture of electrons with energies between ϵ_1 and ϵ_2 . [Such ratios can be obtained from plots of $\sigma_a(\epsilon)$ vs ϵ (see Table V)], and the ratio of the integrated electron attachment rates

$$R_{\langle \epsilon \rangle}^{\langle \epsilon \rangle} = \left\{ \frac{\int_{\epsilon_1}^{\epsilon_2} \alpha w(\langle \epsilon \rangle) d\langle \epsilon \rangle}{\int_{\epsilon_1}^{\epsilon_2} [\alpha w(\langle \epsilon \rangle)]_{\text{max}} d\langle \epsilon \rangle} \right\}. \quad (12)$$

In practical applications (see Part II), where the removal of electrons via attachment is desirable, Eqs. (11) and (12) can provide useful information although it should be kept in mind that it is the overlap of $\sigma_a(\epsilon)$ and

FIG. 1. Electron attachment rate αw vs attaching gas pressure $P_{c-C_4F_6}$ for $c-C_4F_6$ in N_2 ($P_{N_2} = 1000$ torr) for a number of E/P_{298} values (or $\langle \epsilon \rangle$ values).

FIG. 2. Electron attachment rate αw vs pressure P_{N_2} of N_2 for $c-C_4F_6$ ($P_{c-C_4F_6} = 8.86 \times 10^{-5}$ torr) for a number of E/P_{298} values (or $\langle \epsilon \rangle$ values).

$f(\epsilon, E/P)$ which is the most important quantity, i. e., $\int_0^\infty \sigma_a(\epsilon) f(\epsilon, E/P) d\epsilon$.

IV. EXPERIMENTAL RESULTS

A. Electron attachment rates as a function of partial and total pressure

The electron attachment rates for the five perfluorocarbons $c-C_4F_6$, $2-C_4F_6$, $1,3-C_4F_6$, $c-C_3F_8$, and $2-C_3F_8$ investigated were found to be independent of the attaching gas pressure P_{c-F} at constant carrier gas pressure and E/P . The P_{c-F} ranged from 4.3×10^{-5} to 1.46×10^{-3} torr (see Table I). As an example, the αw data for $c-C_4F_6$ are plotted in Fig. 1 as a function of $P_{c-C_4F_6}$ at $P_{N_2} = 1000$ torr. No partial pressure dependence at any E/P value is seen.

The $\alpha w(E/P)$ functions were found also to be independent of the carrier gas pressure P_{N_2} or P_{A_2} in the range of 500 to 2000 torr at constant P_{c-F} and E/P . An example of $\alpha w(E/P)$ vs P_{N_2} is given in Fig. 2 for $P_{c-C_4F_6} = 8.86 \times 10^{-5}$ torr and for various values of E/P .

The attachment rates reported in this paper are those averaged over a number of experimental runs at various attaching and carrier gas pressures as listed in Table I.

B. Electron attachment rates as a function of E/P

In Fig. 3 is shown the dependence of αw on E/P for $c-C_4F_6(O)$, $2-C_4F_6(\bullet)$, and $1,3-C_4F_6(\Delta)$ in mixtures

FIG. 3. Electron attachment rate αw vs E/P_{298} for $c\text{-C}_4\text{F}_6$ (○), $2\text{-C}_4\text{F}_6$ (●), and $1,3\text{-C}_4\text{F}_6$ (▲) in N_2 and Ar. Note that the data for $c\text{-C}_4\text{F}_6$ in Ar were multiplied by a factor of 10 for convenience of display.

with N_2 and Ar. Similar results for $c\text{-C}_4\text{F}_6$ (Δ) and $2\text{-C}_4\text{F}_6$ (■) in N_2 and Ar are shown in Fig. 4.

The main features of the $\alpha w(E/P)$ functions in Figs. 3 and 4 are the maxima at $E/P \approx 0.3 \text{ V cm}^{-1} \text{ torr}^{-1}$ for $c\text{-C}_4\text{F}_6$ and at $E/P \approx 0.7 \text{ V cm}^{-1} \text{ torr}^{-1}$ for $2\text{-C}_4\text{F}_6$ in N_2 . The αw values for $c\text{-C}_4\text{F}_6$, $1,3\text{-C}_4\text{F}_6$, and $2\text{-C}_4\text{F}_6$ are increasing as E/P decreases, and remain high ($\geq 1 \times 10^9 \text{ sec}^{-1} \text{ torr}^{-1}$) for all five perfluorocarbons, even at the highest E/P values used. The measured values of αw for $c\text{-C}_4\text{F}_6$, $2\text{-C}_4\text{F}_6$, $1,3\text{-C}_4\text{F}_6$, $c\text{-C}_4\text{F}_6$, and $2\text{-C}_4\text{F}_6$ in N_2 and Ar are listed, respectively, in Tables II and III as functions of both E/P and $\langle \epsilon \rangle$.

C. Electron attachment rates as a function of $\langle \epsilon \rangle$

Although it is customary to plot the experimental data on αw as a function of E/P for each carrier gas used,

a plot of αw vs $\langle \epsilon \rangle$ is more meaningful, since the latter should be independent of the carrier gas. Tabulated $\langle \epsilon \rangle$ values as a function of E/P for the carrier gases C_2H_4 , N_2 (Ref. 15), and Ar were reported^{5,7,8} earlier.

In Fig. 5, αw vs $\langle \epsilon \rangle$ plots are presented for $c\text{-C}_4\text{F}_6$, $2\text{-C}_4\text{F}_6$, and $1,3\text{-C}_4\text{F}_6$. The "open" points are data taken with N_2 as the carrier gas at 500, 1000, 1500, and 2000 torr, and the "solid" points are data taken with Ar as the carrier gas at 500, 1000, and 1500 torr. They are averages of 15, 11, and 8 runs in N_2 and 9, 4, and 5 runs in Ar, respectively, for $c\text{-C}_4\text{F}_6$ (○, ●), $2\text{-C}_4\text{F}_6$ (○, ●), and $1,3\text{-C}_4\text{F}_6$ (Δ, ▲). The theoretical maximum electron attachment rate (Sec. III.D) is also shown in Fig. 5 as a function of $\langle \epsilon \rangle$ using $f(\epsilon, E/P)$ for N_2 (◇) and Ar (◆). In the same figure, the calculated thermal electron attachment rate at $\langle \epsilon \rangle = \frac{1}{2} kT_{298} \approx 0.038$

FIG. 4. Electron attachment rate αw vs E/P_{298} for $c\text{-C}_4\text{F}_6$ (Δ) and $2\text{-C}_4\text{F}_6$ (■) in N_2 and Ar.

FIG. 5. Electron attachment rate αw vs $\langle \epsilon \rangle$ for $c\text{-C}_4\text{F}_8$ (○, ●, and ◻), $2\text{-C}_4\text{F}_8$ (◊, ◐, and ◑), and $1,3\text{-C}_4\text{F}_8$ (△, ▲, and ▴) in N_2 ("open" points) and in Ar ("solid" points). The points ◊, ◐, and ▴ correspond to the $(\alpha w)_{\text{ther}}$ values at $\langle \epsilon \rangle = \frac{3}{2} kT_{298} = 0.038 \text{ eV}$.

eV (Sec. III. E) is given for $c\text{-C}_4\text{F}_8$ (○), $2\text{-C}_4\text{F}_8$ (◊) and $1,3\text{-C}_4\text{F}_8$ (△). A log-log plot was made to accommodate the wide range of values for both αw and $\langle \epsilon \rangle$.

A plot of αw vs $\langle \epsilon \rangle$ for $c\text{-C}_4\text{F}_8$ (○, ●) and $2\text{-C}_4\text{F}_8$ (△, ▲)

FIG. 6. Electron attachment rate αw vs $\langle \epsilon \rangle$ for $c\text{-C}_4\text{F}_8$ (○, ●, and ◻) and $2\text{-C}_4\text{F}_8$ (△, ▲, and ▴) in N_2 (open points) and Ar (solid points). The points ◊ and ▴ correspond to the $(\alpha w)_{\text{ther}}$ values at $\langle \epsilon \rangle = \frac{3}{2} kT_{298} = 0.038 \text{ eV}$.

FIG. 7. Electron attachment cross section $\sigma_a(\epsilon)$ and monoenergetic electron attachment rate $\alpha w(\epsilon)$ as a function of electron energy ϵ for $2\text{-C}_4\text{F}_8$ in N_2 . $\sigma_a(\epsilon)$ after 495 iterations (V , $R = 6.5 \times 10^{-5}$), after 1386 iterations (○, $R = 4.2 \times 10^{-5}$), after 1980 iterations (△, $R = 3.8 \times 10^{-5}$), and after 2970 iterations (◊, $R = 3.5 \times 10^{-5}$).

is shown in Fig. 6. A similar notation was followed as in Fig. 5. In Fig. 6, the αw values for $c\text{-C}_4\text{F}_8$ and $2\text{-C}_4\text{F}_8$ in N_2 are averages of 4 and 11 runs, respectively, and in Ar averages of 4 and 8 runs, respectively. The $(\alpha w)_{\text{ther}}$ are also shown for $c\text{-C}_4\text{F}_8$ (◊) and $2\text{-C}_4\text{F}_8$ (△).

It is interesting to note that, although the attachment rates for the perfluorocarbons studied were measured independently in N_2 and Ar, the αw vs $\langle \epsilon \rangle$ plots for every molecule investigated in mixtures with the two carrier gases mesh well and form a continuous curve in the E/P range for which the $f(\epsilon, \langle \epsilon \rangle)$ overlap energy-wise, as seen in Figs. 5 and 6. Similar results were reported earlier^{7,8,16,17} (see also Part II).

D. Electron attachment cross section as a function of ϵ

The electron-swarm unfolding technique¹⁰ was applied to the present $\alpha w(\epsilon)$ data for $c\text{-C}_4\text{F}_8$, $2\text{-C}_4\text{F}_8$, $1,3\text{-C}_4\text{F}_8$, $c\text{-C}_4\text{F}_8$, and $2\text{-C}_4\text{F}_8$ in N_2 , and the monoenergetic electron attachment rates $\alpha w(\epsilon)$ were obtained as a function of ϵ . From the so-determined $\alpha w(\epsilon)$ functions, $\sigma_a(\epsilon)$ were calculated through Eq. (3). A typical set of $\alpha w(\epsilon)$ and $\sigma_a(\epsilon)$ functions are given in Fig. 7 for $2\text{-C}_4\text{F}_8$. They were obtained after 2970 iterations (Sec. III. B). The various points for $\sigma_a(\epsilon)$ correspond to different numbers of iterations, as shown in the caption of Fig. 7. It is seen that the change in both the shape and the magnitude of $\sigma_a(\epsilon)$ is very small for large increases in the number of iterations showing convergence.

The $\sigma_a(\epsilon)$ for $c\text{-C}_4\text{F}_8$, $2\text{-C}_4\text{F}_8$, and $1,3\text{-C}_4\text{F}_8$ are shown in Fig. 8 and for $c\text{-C}_4\text{F}_8$ and $2\text{-C}_4\text{F}_8$ in Fig. 9, and are

FIG. 8. Electron attachment cross section $\sigma_a(\epsilon)$ as a function of electron energy ϵ for $c\text{-C}_4\text{F}_8$ ($\bullet$), $2\text{-C}_4\text{F}_8$ ($\circ$), $1,3\text{-C}_4\text{F}_8$ (Δ), and SF_6 ($\square$). The maximum s -wave electron capture is represented by πk^2 .

listed in Table IV. In Figs. 8 and 9, the $\sigma_a(\epsilon)$ functions for SF_6 and $\sigma_{a,\max} = \pi k^2$ are also shown for comparison.

The main features of the $\sigma_a(\epsilon)$ functions in Figs. 8 and 9 are (see also Table V) as follows:

- (1) For all PFC molecules except $c\text{-C}_4\text{F}_8$, $\sigma_a(\epsilon)$ in-

FIG. 9. Electron attachment cross section $\sigma_a(\epsilon)$ as a function of electron energy ϵ for $c\text{-C}_4\text{F}_8$ ($\circ$), $2\text{-C}_4\text{F}_8$ ($\blacktriangle$), and SF_6 ($\square$). The maximum s -wave electron capture is represented by πk^2 .

TABLE IV. $\sigma_a(\epsilon)$ for $c\text{-C}_4\text{F}_8$, $2\text{-C}_4\text{F}_8$, $1,3\text{-C}_4\text{F}_8$, $c\text{-C}_4\text{F}_8$, and $2\text{-C}_4\text{F}_8$.

Electron energy ϵ (eV)	Electron attachment cross section $\sigma_a(\epsilon)$ (10^{-15} cm^2)				
	$c\text{-C}_4\text{F}_8$	$2\text{-C}_4\text{F}_8$	$1,3\text{-C}_4\text{F}_8$	$c\text{-C}_4\text{F}_8$	$2\text{-C}_4\text{F}_8$
0.04	9.57	5.09	10.00	1.13	4.40
0.06	4.23	2.94	5.08	0.99	2.52
0.08	2.60	1.99	3.38	0.97	1.71
0.10	2.16	1.64	2.94	1.07	1.42
0.12	2.06	1.55	2.95	1.23	1.37
0.14	2.00	1.06	3.08	1.43	1.40
0.16	1.85	1.60	3.19	1.65	1.44
0.18	1.66	1.63	2.15	1.96	1.47
0.20	1.22	1.63	2.97	1.98	1.45
0.22	0.89	1.59	2.65	2.03	1.38
0.24	0.63	1.51	2.32	1.99	1.28
0.26	0.44	1.40	1.97	1.89	1.16
0.28	0.30	1.29	1.64	1.78	1.04
0.30	0.21	1.17	1.24	1.64	0.93
0.34	0.11	0.97	0.89	1.42	0.72
0.38	0.07	0.84	0.60	1.29	0.60
0.42	0.05	0.77	0.44	1.21	0.53
0.46	0.047	0.75	0.33	1.18	0.50
0.50	0.046	0.77	0.26	1.16	0.48
0.55	0.053	0.84	0.22	1.13	0.49
0.60	0.062	0.96	0.19	1.00	0.49
0.65	0.068	1.09	0.17	0.92	0.48
0.70	0.073	1.21	0.17	0.78	0.47
0.75	0.070	1.30	0.17	0.62	0.43
0.80	0.058	1.35	0.16	0.46	0.37
0.85	0.041	1.32	0.17	0.32	0.31
0.90	0.028	1.24	0.18	0.23	0.25
0.95	0.017	1.11	0.19	0.15	0.19
1.00	0.008	0.93	0.20	0.09	0.13
1.05	0.003	0.69	0.20	0.05	0.08
1.10		0.46	0.19	0.024	0.045
1.15		0.25	0.17	0.009	0.020
1.20		0.12	0.14	0.003	0.007
1.25		0.04	0.10		0.002
1.30		0.011	0.06		
1.35		0.002	0.028		
1.40			0.011		
1.45			0.004		

creases with decreasing electron energy below 0.1 eV, attaining its maximum value at ~ 0 eV. At 0.04 eV, $\sigma_a(\epsilon)$ for $c\text{-C}_4\text{F}_8$, $2\text{-C}_4\text{F}_8$, $1,3\text{-C}_4\text{F}_8$, and $2\text{-C}_4\text{F}_8$ are very large ($\geq 6 \times 10^{-15} \text{ cm}^2$); at $\epsilon = 0.04$ eV, $\sigma_a(\epsilon)$ for $c\text{-C}_4\text{F}_8$ is $1.1 \times 10^{-15} \text{ cm}^2$.

(2) A well-defined second maximum in $\sigma_a(\epsilon)$ at $\sim 0.2 \pm 0.03$ eV is exhibited for $2\text{-C}_4\text{F}_8$, $1,3\text{-C}_4\text{F}_8$, $c\text{-C}_4\text{F}_8$, and $2\text{-C}_4\text{F}_8$. The $\sigma_a(\epsilon)$ for $c\text{-C}_4\text{F}_8$ exhibits a rather broad shoulder (extending from ~ 0.12 to ~ 0.16 eV) with a possible maximum at ~ 0.14 eV.

(3) A third broad maximum in $\sigma_a(\epsilon)$ is apparent for all PFC molecules at ~ 0.71 , 0.80 , 1.04 , 0.48 , and 0.60 eV for $c\text{-C}_4\text{F}_8$, $2\text{-C}_4\text{F}_8$, $1,3\text{-C}_4\text{F}_8$, $c\text{-C}_4\text{F}_8$, and $2\text{-C}_4\text{F}_8$, respectively. The peak in $\sigma_a(\epsilon)$ for $2\text{-C}_4\text{F}_8$ is the most dominant in this energy region. The peak cross section value for this molecule ($= 1.35 \times 10^{-15} \text{ cm}^2$) is close to $\sigma_{a,\max} = \pi k^2 = 1.50 \times 10^{-15} \text{ cm}^2$ ($\epsilon = 0.8$ eV).

(4) All five PFC molecules have much larger $\sigma_a(\epsilon)$ than SF_6 at $\epsilon \geq 0.4$ eV.

TABLE V. Electron attachment cross section maxima, values of $\sigma_a(\epsilon)$ at these maxima, energy integrated cross sections, autodetachment lifetimes of the parent negative ions at ~ 0.0 eV, and electron affinities for $c\text{-C}_4\text{F}_6$, $2\text{-C}_4\text{F}_6$, $1,3\text{-C}_4\text{F}_6$, $c\text{-C}_4\text{F}_8$, and $2\text{-C}_4\text{F}_8$.

Molecular formula	ϵ_2^a (eV)	$\sigma_a(\epsilon_2)$ (10^{-15} cm 2)	ϵ_3^a (eV)	$\sigma_a(\epsilon_3)$ (10^{-15} cm 2)	$\int_{0.04\text{ eV}}^{1.40\text{ eV}} \sigma_a(\epsilon) d\epsilon$ (10^{-15} eV cm 2)	$R_{0.04\text{ eV}}^{1.40\text{ eV}}$ (%)	Lifetime of C_xF_y^- (μsec)	Electron affinity of C_xF_y (eV)
$c\text{-C}_4\text{F}_6$	~ 0.14	1.96	0.71	0.07	0.53	12.4	6.9 ^c 11.2 ^d	
$2\text{-C}_4\text{F}_6$	0.19	1.64	0.80	1.35	1.31	30.6	8.7 ^e 16.3 ^d	0.7–1.45 ^f
$1,3\text{-C}_4\text{F}_6$	0.17	3.19	1.04	0.20	1.07	25.2		
$c\text{-C}_4\text{F}_8$	0.22	2.03	0.48	1.21	0.98	23.1	12 ^c 14.8 ^e 200 ⁱ	$\geq 0.4^b$
$2\text{-C}_4\text{F}_8$	0.18	1.47	0.59	0.50	0.73	17.1	10.6 ^e 30.6 ^d	$\geq 0.7^b$

^a ϵ_2 and ϵ_3 give the energy position of the second and third maximum in $\sigma_a(\epsilon)$; the first maximum is at ~ 0.0 eV.^bSee Sec. III. F.^cW. T. Naff, C. D. Cooper, and R. N. Compton, J. Chem. Phys. 49, 2784 (1968).^dJ. C. J. Thynne, Dyn. Mass Spectrom. 3, 67 (1972).^eI. Sauer, L. G. Christophorou, and J. G. Carter (to be published).^fP. R. Hammond, J. Chem. Phys. 55, 3468 (1971).^gP. W. Harland and J. C. J. Thynne, Int. J. Mass Spectrom. Ion Phys. 10, 11 (1973).^hC. Lifshitz, T. O. Tiernan, and B. M. Hughes, J. Chem. Phys. 59, 3182 (1973).ⁱJ. M. S. Henis and C. A. Mabie, J. Chem. Phys. 53, 2999 (1970).E. Thermal electron attachment rate $(\alpha w)_{\text{ther}}$

The $(\alpha w)_{\text{ther}}$ values for $c\text{-C}_4\text{F}_6$, $2\text{-C}_4\text{F}_6$, $1,3\text{-C}_4\text{F}_6$, $c\text{-C}_4\text{F}_8$, and $2\text{-C}_4\text{F}_8$ at $\langle \epsilon \rangle = 0.038$ eV, determined via Eq. (10), are shown in column 3 of Table VI and are plotted in Figs. 5 and 6.

If, for simplicity, we use a linear two-point extrapolation of the αw vs $\langle \epsilon \rangle$ plots for the first two measured αw values in N_2 (i. e., at $\langle \epsilon \rangle = 0.046$ and 0.054 eV), the $(\alpha w)_{\text{ther}}$ values so obtained for the five PFC molecules differ from those determined through the unfolding procedure by less than 3% (see Table VI).

TABLE VI. Thermal ($T = 298^\circ\text{K}$) rates for electron attachment to $c\text{-C}_4\text{F}_6$, $2\text{-C}_4\text{F}_6$, $1,3\text{-C}_4\text{F}_6$, $c\text{-C}_4\text{F}_8$, and $2\text{-C}_4\text{F}_8$.

Molecular formula	$(\alpha w)_{\text{ther}}$, ^a at $\langle \epsilon \rangle = 0.046$ eV ($10^3 \text{ sec}^{-1} \text{ torr}^{-1}$)	$(\alpha w)_{\text{ther}}$, ^b at $\langle \epsilon \rangle = 0.038$ eV ($10^3 \text{ sec}^{-1} \text{ torr}^{-1}$)	$(\alpha w)_{\text{ther}}$, ^c at $\langle \epsilon \rangle = 0.038$ eV ($10^3 \text{ sec}^{-1} \text{ torr}^{-1}$)	$(\alpha w)_{\text{ther}}$, ^d lit. ($10^3 \text{ sec}^{-1} \text{ torr}^{-1}$)
$c\text{-C}_4\text{F}_6$	4.20	4.89	4.72	4.54 ^e
$2\text{-C}_4\text{F}_6$	1.68	1.77	1.75	
$1,3\text{-C}_4\text{F}_6$	3.85	4.26	4.15	
				0.28 ^f 0.36 ^g 0.39 ^g $\sim 0.7^h$
$c\text{-C}_4\text{F}_8$	0.45	0.40	0.41	
$2\text{-C}_4\text{F}_8$	1.48	1.56	1.56	1.59 ^e

^aPresent work. Measured αw values in N_2 for $E/P = 0.02 \text{ V cm}^{-1} \text{ torr}^{-1}$ ($\langle \epsilon \rangle = 0.046$ eV) at $T = 298^\circ\text{K}$.^bPresent work. Calculated thermal values from present unfolded $\alpha w(\epsilon)$ data, using Eq. (10).^cPresent work. Determined from two-point extrapolation to $\langle \epsilon \rangle = 0.038$ eV (Sec. III. E).^dReported thermal electron attachment rate constants (Sec. IV. E).^eK. M. Bansal and R. W. Fessenden, J. Chem. Phys. 59, 1760 (1973).^fE. Schultes, Doctoral Thesis, Universität Bonn, Bonn, West Germany (1973); A. A. Christodoulides, E. Schultes, R. Schumacher, and R. N. Schindler, Z. Naturforsch. Teil A 29, 389 (1974).^gF. J. Davis, R. N. Compton, and D. R. Nelson, J. Chem. Phys. 58, 2324 (1973).^hL. G. Christophorou, D. L. McCorkle, and D. Pittman, J. Chem. Phys. 60, 1183 (1974).

V. DISCUSSION

A. Electron attachment reaction mechanism

A large number of polyatomic molecules are known⁵ to attach electrons nondissociatively at low (≤ 2 eV) electron energies for times greater than $1 \mu\text{sec}$. For large and generally symmetric molecules, the excess energy of the captured electron is assumed to be distributed among the many vibrational degrees of freedom of the molecule for a time which is long enough for the negative ion to be detected in a time-of-flight mass spectrometer (TOFMS). Complete stabilization of the transient negative ion with the subsequent formation of a permanent negative ion is possible if the molecular electron affinity is positive (> 0 eV), and the time between collisions is small compared to the autodetachment lifetime τ_a .

The autodetachment lifetimes of $c\text{-C}_4\text{F}_8^+*$, $2\text{-C}_4\text{F}_8^+*$, $c\text{-C}_4\text{F}_8^+*$, and $2\text{-C}_4\text{F}_8^+*$ at ~ 0.0 eV were found¹⁰⁻²² in TOFMS studies to be $> 1 \mu\text{sec}$ (Table V). Although the lifetime of $1,3\text{-C}_4\text{F}_8^+*$ has not yet been measured (it is under investigation²⁰), on the basis of the results on the other two isomers of C_4F_8 , it is expected to be $> 1 \mu\text{sec}$ also.

There is a lack of information on the electron affinities of the perfluorocarbons studied. A lower limit of ≥ 0.4 eV was, however, reported²³ for the electron affinity of $c\text{-C}_4\text{F}_8$ and of ≥ 0.7 eV for $2\text{-C}_4\text{F}_8$. In addition, from comparisons of the absorption onsets of charge transfer bands, it was concluded²⁴ that the electron affinities of O, $2\text{-C}_4\text{F}_8$, $2\text{-C}_4\text{F}_8$, and $c\text{-C}_4\text{F}_8$ should be in the order $E.A.(O) > E.A.(2\text{-C}_4\text{F}_8) > E.A.(2\text{-C}_4\text{F}_8) > E.A.(c\text{-C}_4\text{F}_8)$. If we take as 1.46 eV the electron affinity of the oxygen atom²⁵ and use the lower limits²³ for $c\text{-C}_4\text{F}_8$ and $2\text{-C}_4\text{F}_8$, we predict $0.7 \leq E.A.(2\text{-C}_4\text{F}_8) \leq 1.46$ eV. It is reasonable to assume that the electron affinities of $c\text{-C}_4\text{F}_8$ and $1,3\text{-C}_4\text{F}_8$ are also positive.

A rough estimate of the average time τ_{col} between C_xF_y^+* and N_2 collisions can be found from

$$\nu_{\text{col}} = v \sigma_L n_{\text{N}_2} \quad (13)$$

where v is the relative velocity of C_xF_y^+* and N_2 , n_{N_2} is

the number density of N_2 ($= N_0 P_{\text{N}_2} = 3.241 \times 10^{18} P_{\text{N}_2}$ at $T = 298^\circ\text{K}$), and σ_L is the classical Langevin expression for the cross section for spiralling collisions between C_xF_y^+* and N_2 , given by^{26,27}

$$\sigma_L = \left(\frac{2\pi}{v} \right) \left(\frac{e^2 \alpha}{M_r} \right)^{1/2} \quad (14)$$

In Eq. (14), α is the static polarizability of N_2 ($= 1.76 \times 10^{-24} \text{ cm}^3$) (Ref. 28), e is the electronic charge, and M_r is the reduced mass for the system $\text{C}_x\text{F}_y^+*\text{-N}_2$. From Eqs. (13) and (14), we have

$$\tau_{\text{col}} = \nu_{\text{col}}^{-1} = \frac{1}{2\pi N_0 P_{\text{N}_2}} \left(\frac{M_r}{e^2 \alpha_{\text{N}_2}} \right)^{1/2} \quad (15)$$

For P_{N_2} equal to 500 and 2000 torr at $T = 298^\circ\text{K}$, Eq. (15) gives

$$\tau_{\text{col}} = 15.413 M_r^{1/2}, \text{ for 500 torr,} \quad (16)$$

and

$$\tau_{\text{col}} = 3.853 M_r^{1/2}, \text{ for 2000 torr,} \quad (17)$$

where τ_{col} is given in sec, and M_r is expressed in g. From these calculations, τ_{col} was found equal to $\sim 10^{-10}$ sec [Eq. (16)] and $\sim 2.5 \times 10^{-11}$ sec [Eq. (17)] for the perfluorocarbons under consideration. Since the autodetachment lifetimes of the parent negative ions C_xF_y^+* are $\geq 1 \times 10^{-6}$ sec, τ_{col} is smaller than τ_a by a factor of 10^4 to 10^5 .

The above findings coupled with the observation that the long-lived C_xF_y^+* ions are mainly formed at ~ 0.0 eV in the TOFMS studies suggest that, in the present swarm study, low-energy electrons attach to the C_xF_y molecules nondissociatively, leading to the formation of permanent C_xF_y^+ ions. Recent TOFMS results,²⁰ however, show that it is also possible that thermal and epithermal energy electrons can be captured by these molecules dissociatively. These studies show also that some of the fragment ions can themselves be metastable with $\tau_a > 10^{-6}$ sec.

We can summarize the decay channels of the low-lying negative ion resonances of the perfluorocarbons under discussion, as

The rate constants k_i in expressions (18) are as follows: k_1 for formation of C_xF_y^+* , k_2 for autolocalization, k_3 for dissociation, k_4 for formation of long-lived dissociation fragments, and $k_5[M]$ for collisional stabilization by a third body M ($M = \text{N}_2$, Ar, or C_xF_y) (radiative stabilization may also occur). The symbol (*) indicates that C_xF_y may or may not retain as internal energy some

of the incident electron's kinetic energy and the symbol (') that the outgoing electron may carry less energy than the incident one.

The above reaction scheme (18) predicts

$$\alpha w(\langle \epsilon \rangle) = k_1 \frac{k_3 + k_4 + k_5[M]}{k_2 + k_3 + k_4 + k_5[M]}, \quad (19)$$

where $[M]$ is the concentration of M . Since $\tau_2 (= k_2^{-1})$ is very large ($> 1 \mu\text{sec}$) (the rate constant k_2 for autoionization is very small) and channel (18b) is pressure independent, $\alpha w(\epsilon)$ should be P independent, as is observed experimentally.

B. Negative-ion fragmentation of C_xF_y molecules

Negative ions produced by electron impact on the perfluorocarbons under discussion have been studied by several workers.^{3,20,29-34} It was generally found that "zero-energy" electron impacts result predominantly in the formation of long-lived parent negative ions $C_xF_y^{\cdot-}$, although fragment ions are also produced in many cases. For example, the TOFMS spectrum of $2-C_4F_8$ showed^{3,20} that the formation of $2-C_4F_8^{\cdot-}$ ions at ~ 0.0 eV contributes $> 98\%$ of all negative ions produced in the electron energy up to ~ 10 eV, with the remaining $< 2\%$ consisting of $C_3F_5^{\cdot-}$, F^- , and $CF_3^{\cdot-}$ ions. A similar study^{3,20} for $2-C_4F_8$ showed that this molecule exhibits a far more extensive fragmentation than $2-C_4F_8$, with $\sim 96\%$ relative peak ion intensity for $2-C_4F_8^{\cdot-}$ at ~ 0.0 eV, $\sim 1\%$ for $C_4F_7^{\cdot-}$ at ~ 0.0 eV, and $\sim 3\%$ for F^- , $C_3F_5^{\cdot-}$, $C_4F_8^{\cdot-}$, $CF_3^{\cdot-}$, $C_3F_3^{\cdot-}$, and $C_2F_3^{\cdot-}$ at higher than zero energies (up to ~ 5.4 eV). The observation³⁴ of $C_4F_7^{\cdot-}$ from $2-C_4F_8$ at ~ 0 eV is in accord with the findings of Sauers *et al.*²⁰ A series of nine dissociative capture peaks from $c-C_4F_8$ leading to F^- (five peaks), $CF_3^{\cdot-}$, $C_2F_3^{\cdot-}$, and $C_3F_3^{\cdot-}$ (two peaks) with maxima located from 1.75 to 10.5 eV, in addition to the nondissociative capture peak at 0.03 eV for the formation of $c-C_4F_8^{\cdot-}$, were observed³⁴ and were ascribed to a series of negative ion states.

The higher members of the alicyclic and aromatic series, notably those containing methyl side groups, such as $c-C_6F_{12}$ and $c-C_7F_{14}$, were found³⁵ to undergo extensive fragmentation, although the formation of the parent negative ions remained high.

C. Electron attachment cross sections

The electron attachment cross section for $c-C_4F_8$ showed three maxima (Fig. 9) in the energy range ~ 0 to ~ 1.5 eV: a "zero-energy" peak with $\sigma_a(\epsilon = 0.03 \text{ eV}) = 1.17 \times 10^{-15} \text{ cm}^2$, a dominant peak at 0.22 eV with $\sigma_a(\epsilon = 0.22 \text{ eV}) = 2.03 \times 10^{-15} \text{ cm}^2$, and a broad shoulder extending from 0.4 to 0.6 eV with $\sigma_a(\epsilon = 0.5 \text{ eV}) \approx 1.16 \times 10^{-15} \text{ cm}^2$. Similar results were found for $c-C_4F_8$, $2-C_4F_8$, $1,3-C_4F_8$ (Fig. 8), and $2-C_4F_8$ (Fig. 9 and Table V).

The formation of negative ions from $c-C_4F_8$ at low-electron energies has been studied by several workers.^{21,29-32} The energy dependence of the total electron attachment cross section showed³⁰ a complicated structure in the energy range from ~ 0 to 12 eV, with the largest cross section value ($= 2.14 \times 10^{-17} \text{ cm}^2$) at the resonance maximum close to 0 eV. The $C_4F_8^{\cdot-}$ ion current was not normalized, however, by the electron current which considerably underestimates¹⁸ the reported³⁰ $\sigma_a(\epsilon)$, and the absence of a mass analysis of the ions formed hinders the interpretation of these data. The $c-C_4F_8^{\cdot-}$ ion was found²¹ to be formed at ~ 0 eV. This ion was responsible for virtually all of the ion current intensity measured. The observed²¹ symmetrical

resonance peak reached a maximum value at 0.45 ± 0.1 eV. Based on the relative peak intensities of $c-C_4F_8^{\cdot-}$ and $SF_6^{\cdot-}$ and a value for the electron attachment cross section for SF_6 at $\epsilon = 0.05$ eV equal to $1.17 \times 10^{-14} \text{ cm}^2$,³⁵ it was estimated²¹ that $\sigma_{c-C_4F_8}(\epsilon = 0.05 \text{ eV}) = 1.3 \times 10^{-16} \text{ cm}^2$. This estimate is an order of magnitude smaller than the value of $1.06 \times 10^{-15} \text{ cm}^2$ at $\epsilon = 0.05$ eV from the present work.

The energy dependence of $\sigma_a(\epsilon)$ for $c-C_4F_8$, $2-C_4F_8$, $1,3-C_4F_8$, $c-C_4F_8$, and $2-C_4F_8$ (Figs. 8 and 9) showed three negative ion resonances at electron energies below ~ 1.3 eV. Many molecules were found to possess a multiplicity of negative ion resonances in the subexcitation energy region. This was clearly illustrated by the recent data¹⁴ on the production of Cl^- from chloroethylenes and chloroethanes. For both groups of molecules, five negative ion states were identified¹⁴ below ~ 2 eV and were associated with orbitals dominated by the p orbitals of the chlorine atoms.

It is interesting to compare the $\sigma_a(\epsilon)$ for $c-C_4F_8$, $2-C_4F_8$, $1,3-C_4F_8$, $c-C_4F_8$, and $2-C_4F_8$ with that for SF_6 . The $\sigma_a(\epsilon)$ for the former extend to much higher energies than the $\sigma_a(\epsilon)$ for SF_6 , which drops sharply above ~ 0.4 eV (Figs. 8 and 9). This behavior of $\sigma_a(\epsilon)$ as a function of ϵ seems to explain some features of the breakdown strength behavior of SF_6 in comparison to that of the perfluorocarbons. The breakdown strength of the five PFC studied was found¹⁻⁴ to be 1.4 to 2.2 times larger than that for SF_6 under similar experimental conditions, and to hold better in nonuniform fields than that for SF_6 (see discussion in Refs. 1 to 4 and Part II).

D. Thermal electron attachment rates

Thermal electron attachment rate constants k_{ther} (in $\text{cm}^3 \text{sec}^{-1} \text{molecule}^{-1}$) for $c-C_4F_8$, $c-C_4F_8$, and $2-C_4F_8$ were determined by a microwave conductometric method combined with the pulse radiolysis technique and were found³⁶ equal to 1.4×10^{-7} , 1.2×10^{-8} , and $4.9 \times 10^{-8} \text{ cm}^3 \text{sec}^{-1} \text{molecule}^{-1}$, respectively, in mixtures with propane at 25°C . To convert these thermal rate constants to thermal attachment rates (αw), the following well-known relationship [equivalent to Eq. (1)] is used

$$\alpha w = N_0 \int_0^\infty v \sigma_a(v) f(v) dv = N_0 \langle v \sigma_a(v) \rangle \approx N_0 k \quad (20)$$

or

$$(\alpha w)_{\text{ther}} = 3.241 \times 10^{16} k_{\text{ther}} \text{ (in sec}^{-1} \text{ torr}^{-1}) \quad (21)$$

at $T = 298^\circ\text{K}$. The values of $(\alpha w)_{\text{ther}}$ obtained from Eq. (21) by using the literature data³⁶ on k_{ther} for $c-C_4F_8$, $c-C_4F_8$, and $2-C_4F_8$ are compared in Table VI with the present measurements for these molecules and are seen to be in excellent agreement.

A modified time-of-flight electron swarm method, called the drift-dwell-drift technique, was used³⁷ to obtain k_{ther} for $c-C_4F_8$ which was found equal to $1.11 \times 10^{-8} \text{ cm}^3 \text{sec}^{-1} \text{molecule}^{-1}$ ($= 2.6 \times 10^8 \text{ sec}^{-1} \text{ torr}^{-1}$). From time-dependent measurements at constant electron scavenger concentration, a k_{ther} value of $0.9 \times 10^{-8} \text{ cm}^3 \text{sec}^{-1} \text{molecule}^{-1}$ ($= 2.92 \times 10^8 \text{ sec}^{-1} \text{ torr}^{-1}$) was re-

ported^{38,39} for $c\text{-C}_4\text{F}_8$ by using the electron cyclotron resonance (ECR) technique. Since the present and the reported thermal values of the electron attachment rate are averages over several runs at various pressures, the agreement of all the data is considered to be good. No such data were found in the literature for $2\text{-C}_4\text{F}_8$ and $1,3\text{-C}_4\text{F}_8$.

An earlier electron swarm study⁴⁰ of $c\text{-C}_4\text{F}_8$ in N_2 at 400 torr gave $(\alpha w)_{\text{thor}} \approx 7 \times 10^5 \text{ sec}^{-1} \text{ torr}^{-1}$, which is higher than the present ($\approx 4 \times 10^5 \text{ sec}^{-1} \text{ torr}^{-1}$) value. It is noted, however, that the overall energy dependence of αw and the position of the maxima of the $\alpha w(\epsilon)$ and $\sigma(\epsilon)$ functions are in excellent agreement with the present work. It is believed that the discrepancy (by a factor of ~ 1.5) in the magnitude of the $\alpha w(\epsilon)$ functions between the earlier⁴⁰ and the present data is due to an error in the measurement of the pressure of $c\text{-C}_4\text{F}_8$ in the earlier study.⁴⁰

E. Effect of molecular structure on the electron attachment to perfluorocarbons

1. Open-chain saturated PFC molecules

Observations of electron attachment to the saturated perfluorocarbons CF_4 ,^{37,41} C_2F_6 ,^{37,41} C_3F_8 ,^{37,41,42} and $n\text{-C}_4\text{F}_{10}$ (Ref. 41) with an open-chain structure shows that their thermal attachment rates are several orders of magnitude smaller than those measured for the PFC molecules studied in this and the following paper. The $(\alpha w)_{\text{thor}}$ was reported^{37,41,42} to be $< 10^5 \text{ sec}^{-1} \text{ torr}^{-1}$ for CF_4 and C_2F_6 , $\leq 10^4 \text{ sec}^{-1} \text{ torr}^{-1}$ for C_3F_8 , and $\sim 3 \times 10^5 \text{ sec}^{-1} \text{ torr}^{-1}$ for $n\text{-C}_4\text{F}_{10}$. As the molecular size (chain length) increases, $(\alpha w)_{\text{thor}}$ increases.

It should be noted here, however, that although $(\alpha w)_{\text{thor}}$ for the above saturated PFC molecules are very small, they may be significantly larger at higher electron energies. This is the case for C_3F_8 for which the electron attachment rate increases by a factor of $\sim 10^2$ in going from thermal energy to $\epsilon = 0.85 \text{ eV}$. Thus, for a complete picture of the electron scavenging efficiency of a molecule, it is necessary that the dependence of the attachment rate and cross section on the electron energy is studied.

It seems from the above findings that, as the molecular structure becomes more symmetric and compact in open-chain saturated perfluorocarbons (i.e., in going from $n\text{-C}_4\text{F}_{10}$ to CF_4), the electron capturing efficiency decreases.

2. Open-chain unsaturated PFC molecules

With the introduction of double or triple bonds in the chain of the saturated perfluorocarbons, $\alpha w(\epsilon)$ increases drastically. Thus, the one double-bonded $2\text{-C}_4\text{F}_8$, the two double-bonded $1,3\text{-C}_4\text{F}_8$, and the one triple-bonded $2\text{-C}_4\text{F}_6$ showed significant increases in the thermal electron attachment rate, reaching values of up to $4 \times 10^9 \text{ sec}^{-1} \text{ torr}^{-1}$.

The $(\alpha w)_{\text{thor}}$ for the unsaturated double-bonded C_2F_4 was reported⁴¹ to be larger by a factor of $\sim 10^4$ than that for the saturated single-bonded C_2F_6 compound although

the observed large $(\alpha w)_{\text{thor}}$ value ($\sim 1 \times 10^6 \text{ sec}^{-1} \text{ torr}^{-1}$) for C_2F_4 might be due⁴¹ to impurities. No other electron attachment data on open-chain unsaturated perfluorocarbons seem to exist.

3. Cyclic PFC molecules

In this category of perfluorocarbons, we include three-, four-, five-, and six-carbon ring molecules, with or without double bonds. The present work (see also Part II) indicates that the introduction of double bonds in cyclic perfluorocarbons is not so significant as in the open-chain unsaturated PFC molecules. For example, $c\text{-C}_4\text{F}_8$ with one double bond and $c\text{-C}_4\text{F}_8$ with only single bonds did not show appreciable differences in the magnitude of the electron attachment rate in the energy range studied.

A reported³⁸ lower limit ($< 1 \times 10^5 \text{ sec}^{-1} \text{ torr}^{-1}$) for $(\alpha w)_{\text{thor}}$ for the cyclic $c\text{-C}_3\text{F}_6$ is low compared to the $(\alpha w)_{\text{thor}}$ values (between 4×10^8 and $2 \times 10^{10} \text{ sec}^{-1} \text{ torr}^{-1}$) for the cyclic perfluorocarbons $c\text{-C}_3\text{F}_6$, $c\text{-C}_4\text{F}_8$, $c\text{-C}_5\text{F}_{10}$, $c\text{-C}_6\text{F}_{12}$, C_7F_{14} , and C_8F_{16} of the present and the following (Part II) paper.

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APPENDIX B

Electron Attachment to Perfluorocarbon Compounds.

II. $\text{c-C}_5\text{F}_8$, $\text{c-C}_6\text{F}_{10}$, $\text{c-C}_6\text{F}_{12}$, C_7F_8 , and C_8F_{16} ;
Relevance to Gaseous Dielectrics

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Electron attachment to perfluorocarbon compounds. II. $c\text{-C}_5\text{F}_8$, $c\text{-C}_6\text{F}_{10}$, $c\text{-C}_6\text{F}_{12}$, C_7F_8 , and C_8F_{16} : Relevance to gaseous dielectrics^{a)}

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Electron attachment rates αw as a function of the pressure-reduced electric field have been measured for $c\text{-C}_5\text{F}_8$ (perfluorocyclopentene), $c\text{-C}_6\text{F}_{10}$ (perfluorocyclohexene), $c\text{-C}_6\text{F}_{12}$ (perfluoro-1,2-dimethylcyclobutane), C_7F_8 (perfluorotoluene), and C_8F_{16} (perfluoro-1,3-dimethylcyclohexane). The thermal values $(\alpha w)_{\text{th}}$ of the attachment rate for these compounds are 12.8, 12.9, 5.0, 9.2, and $2.4 \times 10^9 \text{ sec}^{-1} \text{ Torr}^{-1}$, respectively. The electron attachment cross sections $\sigma_a(\epsilon)$ as functions of the electron energy ϵ have been determined using the swarm-unfolding technique; they show distinct structure at $\epsilon < 1.5 \text{ eV}$. The electron attachment properties for the perfluorocarbons (PFCs) studied in this and the preceding paper depend strongly on the molecular structure. Thus (i) open-chain saturated PFCs do not attach electrons as efficiently as the unsaturated PFCs; (ii) for saturated PFCs an increase in molecular size (chain length) increases αw ; (iii) the presence of multiple bonds in the molecule dramatically increases the magnitude of αw for the saturated open-chain PFCs, but it has only a small effect for cyclic PFCs; (iv) the cyclic nature of the PFCs seems to increase greatly $\sigma_a(\epsilon)$; and (v) for single-bonded cyclic PFCs, substitution of CF_3 groups for F atoms increases $(\alpha w)_{\text{th}}$ more than does an increase in molecular size; in double-bonded cyclic compounds increase in ring size increases $\sigma_a(\epsilon)$ at thermal energies. The PFCs studied in this and the preceding paper have higher dielectric strengths than SF_6 . This improvement in dielectric strength can be attributed to their large $\sigma_a(\epsilon)$ over a wider energy range (to $\sim 1.5 \text{ eV}$). Their use as unitary gases and/or as additives to multicomponent gas mixtures is discussed.

I. INTRODUCTION

In the preceding paper (Part I), we discussed the electron attaching properties of perfluorinated four-carbon compounds and the significance of knowledge of the electron attachment rates and cross sections to the understanding of the interactions of these molecules with low-energy electrons. The energy dependence of the electron attachment cross sections, for example, provides information about the negative ion states of these molecules. The magnitude and energy dependence of the cross sections for formation as well as for the fragmentation and decay channels of these negative ion states provides information as to the influence of structure on the details of the electron-polyatomic molecule interaction in the extreme low-energy regime.

In this paper, we extend the study to perfluorocarbon compounds with five or more carbon atoms and discuss the relevance of the measured attachment rates and calculated cross sections as a function of electron energy ϵ to the use of these perfluorinated compounds as gaseous dielectrics. The perfluorocarbons studied in this and the preceding paper can be used both as unitary dielectric gases and/or as additives to multicomponent gas mixtures in combination with other gases which may themselves not attach electrons.¹⁻⁶ The knowledge of electron attachment cross sections can serve as a guide

to choosing appropriate components for multicomponent gas mixtures.¹⁻⁶

II. EXPERIMENTAL SECTION

The experimental and analytical techniques employed and the apparatus used to measure the electron attachment rates for the compounds studied in this paper are identical to those used and discussed in the preceding paper, and they will not be discussed further. The sources of error in our measurements have been discussed in the preceding paper and that discussion applies here as well. In Table I are listed the compounds investigated in this paper along with their structural formulas, boiling points, and range of partial pressures used. The quoted purities of these compounds, as supplied by Columbia Organic Chemical Company, are 97+%.

III. RESULTS

A. Electron attachment rates as a function of E/P and ϵ

In Tables II and III are listed the measured electron attachment rates as a function of E/P (the pressure-reduced electric field) for the five compounds studied using nitrogen (Table II) and argon (Table III) as the carrier gas. The mean energies $\langle \epsilon \rangle$ of the electrons in each gas as a function of E/P are listed in these tables also.

Figures 1 and 2 show, respectively, the electron attachment rates αw as a function of $\langle \epsilon \rangle$ with nitrogen and argon as the carrier gas. They are remarkably close in the range where the computed $\langle \epsilon \rangle$'s overlap. This close agreement of the electron attachment rates measured using the two carrier gases for all of the per-

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TABLE I. Nomenclature, molecular and structural formulas, pressure ranges used, and boiling and freezing points for $c\text{-C}_5\text{F}_8$, $c\text{-C}_6\text{F}_{10}$, $c\text{-C}_6\text{F}_{12}$, C_7F_8 , and C_8F_{16} .

Perfluorocarbon	Molecular formula	Structural formula	$P_{c,F}$ in N_2 ^a (10^{-5} torr)	$P_{c,F}$ in Ar ^b (10^{-5} torr)	Boiling point (°C)	Freezing point (°C)
Perfluorocyclopentene	$c\text{-C}_5\text{F}_8$		(16) ^c 4.53–43.39	(9) 8.73–17.62	25 ^d 33 to 35 ^e	
Perfluorocyclohexene	$c\text{-C}_6\text{F}_{10}$		(20) 1.0–7.73	(2) 9.68	54 ^d	
Perfluoro-1,2-dimethylcyclobutane	$c\text{-C}_6\text{F}_{12}$		(19) 3.94–9.09	(8) 3.84–9.73		
Perfluorotoluene	C_7F_8		(7) 1.46–4.83	(1) 4.75	80.5 ^f 103 ^d	–98 ^f
Perfluoro-1,3-dimethylcyclohexane	C_8F_{16}		(8) 5.90–9.70	(9) 7.88–17.49	100.2 ^d 101.5 ^e 102.1 ^e	–55 ^e –70 ^f

^aThe pressures of N_2 employed are 500, 1000, 1500, and 2000 torr.^bThe pressures of Ar employed are 500, 1000, and 1500 Torr.^cThe numbers in parentheses give the number of independent runs made in N_2 or Ar .^dE. R. Larsen, *Fluorine Chem. Rev.* 3, 1 (1969).^eT. J. Brice, *Fluorine Chemistry*, edited by J. H. Simons (Academic, New York, 1950), Vol. I, Chap. 13, p. 452.^fJ. B. Irving and D. T. Jamieson, *J. Fluorine Chem.* 5, 440 (1975).^gJ. H. Simons and J. T. Brice, *Fluorine Chemistry*, edited by J. H. Simons (Academic, New York, 1954), Vol. II, Chap. 6, p. 105.TABLE II. Electron attachment rates for $c\text{-C}_5\text{F}_8$, $c\text{-C}_6\text{F}_{10}$, $c\text{-C}_6\text{F}_{12}$, C_7F_8 , and C_8F_{16} in N_2 .

E/F_{288} ($\text{V cm}^{-1} \text{ torr}^{-1}$)	$\langle \epsilon \rangle$ (eV)	uw in N_2 ($10^9 \text{ sec}^{-1} \text{ torr}^{-1}$)					$(\alpha w)_{\text{max}}^a$ ($10^9 \text{ sec}^{-1} \text{ torr}^{-1}$)
		$c\text{-C}_5\text{F}_8$	$c\text{-C}_6\text{F}_{10}$	$c\text{-C}_6\text{F}_{12}$	C_7F_8	C_8F_{16}	
0.02	0.046	11.62	11.88	4.73	8.42	2.49	13.25
0.03	0.054	10.72	10.81	4.51	7.71	2.55	12.55
0.04	0.064	9.46	9.89	4.33	7.21	2.65	11.44
0.05	0.075	8.47	8.91	4.21	6.76	2.77	10.60
0.06	0.087	7.58	7.98	4.08	6.33	2.85	9.70
0.07	0.099	6.88	7.28	3.98	5.91	2.96	9.05
0.10	0.131	6.47	5.91	3.79	5.12	3.12	7.85
0.15	0.181	4.18	4.58	3.47	4.15	3.16	0.00
0.20	0.230	3.42	3.73	3.16	3.48	2.96	5.85
0.25	0.285	2.90	3.17	2.87	2.98	2.74	5.30
0.35	0.376	2.23	2.38	2.38	2.36	2.33	4.60
0.50	0.490	1.67	1.73	1.86	1.80	1.84	3.97
0.60	0.550	1.48	1.50	1.64	1.59	1.63	3.72
0.80	0.646	1.24	1.19	1.36	1.31	1.33	3.40
1.00	0.715	1.09	1.08	1.20	1.18	1.18	3.20
1.20	0.764	0.99	0.91	1.05	1.08	1.06	3.08
1.40	0.803	0.90	0.81	0.98	1.02	0.97	3.00
1.70	0.846	0.85	0.68	0.88	0.95	0.86	2.93

^aThe values of $(\alpha w)_{\text{max}}$ were obtained using Eq. (9) of Part I and the f_{N_2} (ϵ , $\langle \epsilon \rangle$) functions for N_2 (see Sec. II.D, Part I).

TABLE III. Electron attachment rates for $c\text{-C}_5\text{F}_8$, $c\text{-C}_6\text{F}_{10}$, $c\text{-C}_6\text{F}_{12}$, C_7F_8 , and C_8F_{16} in Ar.

E/P_{298} (V cm ⁻¹ torr ⁻¹)	$\langle \epsilon \rangle$ (eV)	αW in Ar (10 ⁹ sec ⁻¹ torr ⁻¹)					$(\alpha W)_{\text{max}}^a$ (10 ⁹ sec ⁻¹ torr ⁻¹)
		$c\text{-C}_5\text{F}_8$	$c\text{-C}_6\text{F}_{10}$	$c\text{-C}_6\text{F}_{12}$	C_7F_8	C_8F_{16}	
0.010	0.498	1.64	1.54	1.78	1.61	1.91	3.89
0.015	0.570	1.43	1.31	1.56	1.41	1.69	3.63
0.02	0.641	1.27	1.15	1.39	1.28	1.46	3.39
0.03	0.752	1.08	0.97	1.15	1.10	1.23	3.13
0.04	0.848	0.93	0.83	0.97	0.95	1.04	2.90
0.05	0.935	0.81	0.73	0.84	0.84	0.90	2.81
0.06	1.012	0.72	0.66	0.74	0.75	0.79	2.70
0.10	1.285	0.51	0.47	0.53	0.54	0.57	2.38
0.15	1.559	0.38	0.36	0.42	0.38	0.45	2.11
0.20	1.797	0.31	0.30	0.37	0.32	0.37	1.87
0.25	2.008	0.27	0.26	0.33	0.26	0.33	1.66
0.30	2.197	0.23	0.23	0.30	0.24	0.29	1.50
0.40	2.526	0.19	0.19	0.25	0.19	0.24	1.25
0.50	2.808	0.17	0.16	0.22	0.17	0.21	1.08

^aThe values of $(\alpha W)_{\text{max}}$ were obtained using Eq. (9) of Part I and the $f_{\text{Ar}}(\epsilon, \langle \epsilon \rangle)$ functions for Ar (see Sec. III. D, Part I).

fluorocarbon compounds studied indicates that the distribution of electron energies in the overlapping mean energy range is similar for both carrier gases. It also demonstrates the consistency of the data and the mean energy scales as established by the two carrier gases (N_2 and Ar). The attachment rates were found to be independent both of the attaching and the carrier gas pressures. The lack of pressure dependence indicates that all of the ions which are formed in the collision of slow electrons with the perfluorocarbon molecules under study are stabilized at the pressures employed and that the measured attachment rates are the total electron capture rates for these compounds.

The magnitudes of the electron attachment rates for all the perfluorocarbons studied in this paper is largest at near-thermal energies and decreases with increasing $\langle \epsilon \rangle$ above thermal energy, except for C_8F_{16} for which the attachment rate has a maximum at $\langle \epsilon \rangle \approx 0.18$ eV.

B. Electron attachment cross sections as a function of ϵ

Using the swarm unfolding technique,¹ we have calculated the electron attachment cross sections $\sigma_a(\epsilon)$ for these compounds as is discussed in Part I. These are plotted as a function of ϵ in Figs. 3 and 4 and are listed

FIG. 1. Electron attachment rate αW vs $\langle \epsilon \rangle$ for $c\text{-C}_5\text{F}_8$ (○, ●) and $c\text{-C}_6\text{F}_{10}$ (△, ▲) in N_2 (open points) and in Ar (solid points).

FIG. 2. Electron attachment rate αW vs $\langle \epsilon \rangle$ for $c\text{-C}_6\text{F}_{12}$ (Δ , $\bullet$), C_7F_8 ($\circ$, $\bullet$), and C_8F_{16} ($\square$, $\bullet$) in N_2 (open points) and in Ar (solid points).

in Table IV. The attachment cross sections for SF_6 and the maximum cross section for s -wave capture are also plotted in each of the figures for comparison.

Several features of $\sigma_a(\epsilon)$ deserve comment (see Figs. 3 and 4 and Tables IV and V). For all the nonaromatic

perfluorocarbons, three negative ion resonances (NIR's) can be identified below ~ 1 eV. For the aromatic compound perfluorotoluene (C_7F_8), at least two NIR's are detected, and this is consistent with earlier observations by Gant and Christophorou⁸ on perfluorobenzene.

FIG. 3. Electron attachment cross section $\sigma_a(\epsilon)$ as a function of electron energy ϵ for $c\text{-C}_5\text{F}_8$ ($\circ$), $c\text{-C}_6\text{F}_{10}$ (Δ), and SF_6 ($\square$). The maximum s -wave electron capture is represented by $\pi\lambda^2$.

FIG. 4. Electron attachment cross section $\sigma_a(\epsilon)$ as a function of electron energy ϵ for $c\text{-C}_6\text{F}_{12}$ (Δ), C_7F_8 ($\bullet$), C_8F_{16} ($\square$) and SF_6 ($\diamond$). The maximum s -wave electron capture is represented by $\pi\lambda^2$.

TABLE IV. $\sigma_a(\epsilon)$ for $c\text{-C}_3\text{F}_8$, $c\text{-C}_6\text{F}_{10}$, $c\text{-C}_8\text{F}_{12}$, C_7F_8 , and C_8F_{16} .

Electron energy ϵ (eV)	Electron attachment cross section $\sigma_a(\epsilon)$ (10^{-15} cm^2)				
	$c\text{-C}_3\text{F}_8$	$c\text{-C}_6\text{F}_{10}$	$c\text{-C}_8\text{F}_{12}$	C_7F_8	C_8F_{16}
0.04	39.82	40.34	13.43	22.43	7.20
0.06	16.51	17.66	7.94	12.58	5.53
0.08	6.43	8.18	5.74	8.80	4.74
0.10	3.60	4.80	5.09	7.38	4.64
0.12	2.64	3.58	5.03	6.74	4.86
0.14	2.38	3.17	5.13	6.15	5.20
0.16	2.49	3.20	5.16	5.45	5.48
0.18	2.73	3.34	5.04	4.61	5.60
0.20	3.04	3.60	4.73	3.89	5.36
0.22	3.25	3.69	4.30	3.20	4.92
0.24	3.35	3.61	3.82	2.62	4.34
0.26	3.27	3.35	3.36	2.17	3.73
0.28	2.97	2.93	2.91	1.81	3.15
0.30	2.56	2.44	2.51	1.54	2.64
0.34	1.64	1.53	1.89	1.17	1.89
0.38	0.96	0.92	1.48	0.94	1.45
0.42	0.59	0.61	1.21	0.81	1.20
0.46	0.39	0.43	1.03	0.71	1.04
0.50	0.28	0.34	0.89	0.64	0.92
0.55	0.22	0.30	0.77	0.57	0.81
0.60	0.23	0.32	0.65	0.52	0.66
0.65	0.22	0.31	0.57	0.46	0.58
0.70	0.24	0.32	0.50	0.42	0.49
0.75	0.26	0.30	0.41	0.38	0.40
0.80	0.30	0.26	0.32	0.34	0.31
0.85	0.34	0.19	0.25	0.31	0.23
0.90	0.38	0.13	0.19	0.29	0.18
0.95	0.42	0.08	0.15	0.28	0.13
1.00	0.43	0.04	0.10	0.26	0.10
1.05	0.40	0.013	0.06	0.25	0.06
1.10	0.32	0.003	0.033	0.24	0.04
1.15	0.22		0.014	0.23	0.02
1.20	0.12		0.005	0.21	0.007
1.25	0.05		0.001	0.20	0.002
1.30	0.017			0.18	
1.35	0.004			0.16	
1.40	0.001			0.13	
1.45				0.11	
1.50				0.08	
1.55				0.06	
1.60				0.04	

Except for perfluorotoluene, the $\sigma_a(\epsilon)$ functions have maxima at $\sim 0.15\text{--}0.3$ eV in addition to those at thermal energies and $\sim 0.7\text{--}1.1$ eV. The attachment cross sections for all five compounds studied are $\geq 6 \times 10^{-15} \text{ cm}^2$ at $\epsilon < 0.05$ eV and remain large ($\geq 1 \times 10^{-16} \text{ cm}^2$) in the energy range to ~ 0.8 eV.

C. Thermal ($T \sim 298^\circ\text{K}$) values of the electron attachment rates

Thermal values $(\alpha w)_{\text{ther}}$ of the electron attachment rates as calculated (see Part I) by a convolution of a Maxwellian ($T = 298^\circ\text{K}$) electron energy distribution function with the calculated $\sigma_a(\epsilon)$ functions are listed in Table VI. Also listed in Table VI are the thermal attachment rates determined by a linear extrapolation to $\langle \epsilon \rangle = 0.038$ eV—along with some measured values by Davis *et al.*⁹ The values of $(\alpha w)_{\text{ther}}$ for $c\text{-C}_3\text{F}_8$ and $c\text{-C}_6\text{F}_{10}$ are the largest ever reported. The data of Davis *et al.*⁹ on $c\text{-C}_6\text{F}_{10}$ and C_7F_8 are relatively close to our

results, but their $(\alpha w)_{\text{ther}}$ value for $c\text{-C}_3\text{F}_8$ is a factor of 3 lower. We have no explanation for this large difference.

IV. DISCUSSION

A. Effect of molecular structure on the positions of the negative ion resonances and their respective cross sections

In the preceding paper (Part I), we discussed the effect of molecular structure on the electron attachment properties of perfluorinated four-carbon compounds. The salient features of that discussion are as follows:

(i) Open-chain saturated perfluorocarbons do not attach electrons as efficiently as unsaturated ones.

(ii) For saturated perfluorocarbons, an increase in molecular size (chain length) increases the electron attachment rate.

(iii) The presence of multiple bonds in the molecule dramatically increases the magnitude of the electron attachment rate for saturated open-chain molecules, but it has only a small effect for cyclic perfluorocarbons.

(iv) The cyclic nature of the perfluorocarbons seems to increase greatly their electron capture cross sections.

In this section, we expand on the effects of the perfluorocarbon structure on their electron attaching properties by considering the data on all ten perfluorocarbons studied in Parts I and II.

For all ten aliphatic perfluorocarbons studied in this and the preceding paper, three negative ion resonances have been detected at $\epsilon \leq 1.5$ eV. The structural features of these perfluorocarbons have been systematically varied to determine their effect on the positions and the respective cross sections of the NIR states. Thus, we have altered the cyclobutane ($c\text{-C}_4\text{F}_8$) structure to include a pair of CF_3 groups to give $c\text{-C}_6\text{F}_{12}$ and then we expanded it to a cyclohexane structure (C_6F_{12}). The similarity of $\sigma_a(\epsilon)$ for $c\text{-C}_6\text{F}_{12}$ and C_6F_{12} shows that the size of singly bonded cyclic compounds does not have a strong influence on the energy position of the NIR's or on the magnitude of their respective $\sigma_a(\epsilon)$. In going from $c\text{-C}_4\text{F}_8$ to the more complex compounds, two aspects have been introduced: (i) increased complexity and (ii) addition of CF_3 groups. If, as the $c\text{-C}_6\text{F}_{12}$, C_6F_{12} comparison indicates, increased complexity is not a major factor, then we can attribute the significant increase in the magnitude of $\sigma_a(\epsilon)$ for $c\text{-C}_6\text{F}_{12}$ and C_6F_{12} over that of $c\text{-C}_4\text{F}_8$ at thermal energies to the presence of the CF_3 groups in these structures.

Additionally, we have taken a double-bonded cyclic compound and enlarged it progressively as in the series $c\text{-C}_4\text{F}_8$, $c\text{-C}_5\text{F}_8$, and $c\text{-C}_6\text{F}_{10}$. In this group of perfluorocarbons, increasing the complexity increases the magnitude of the "zero-energy" cross section and the cross section at ~ 0.2 eV. The magnitude of $\sigma_a(\epsilon)$ at higher energies is also increased for $c\text{-C}_5\text{F}_8$ and $c\text{-C}_6\text{F}_{10}$ relative to $c\text{-C}_4\text{F}_8$, but the $c\text{-C}_5\text{F}_8$ cross section is larger at higher energies than the $c\text{-C}_6\text{F}_{10}$ cross section. It may be concluded that in this series of compounds the attachment cross section increases with increasing molecular size.

TABLE V. Electron attachment cross section maxima, values of $\sigma_a(\epsilon)$ at these maxima, energy integrated cross sections, autodetachment lifetimes of the parent negative ions at ~ 0.0 eV, and electron affinities for $c\text{-C}_2\text{F}_8$, $c\text{-C}_3\text{F}_{10}$, $c\text{-C}_6\text{F}_{12}$, C_7F_8 , and C_8F_{16} .

Molecular formula	ϵ_1^a (eV)	$\sigma_a(\epsilon_2)$ (10^{-15} cm 2)	ϵ_3^a (eV)	$\sigma_a(\epsilon_3)$ (10^{-15} cm 2)	$\int_{0.04}^{1.40} \sigma_a(\epsilon) d\epsilon$ (10^{-15} eV cm 2)	$RJ_{0.04}^{1.40}$ eV b (%)	Lifetime of $\text{C}_x\text{F}_y^{--}$ (μsec)	Electron affinity of C_xF_y (eV)
SF_6	0.31	3.06			1.17	27.5	25^{2c} $25\text{--}35^a$ 66^d	$\geq 0.6 \pm 0.1^d$
$c\text{-C}_2\text{F}_8$	0.24	3.35	0.99	0.43	1.83	43.0	26.2^a 50.0^b	
$c\text{-C}_6\text{F}_{10}$	0.22	3.69	0.71	0.33	1.93	45.4	106^a 113^b	$\geq 1.4 \pm 0.3^d$
$c\text{-C}_6\text{F}_{12}$	0.16	5.16			1.83	43.0	130^a 450^b	
C_7F_8			~ 1.1	0.24	2.01	47.2	12.2^b 37.8^a	$\geq 1.7 \pm 0.3^d$
C_8F_{16}	0.18	5.60			1.76	41.5		

^a ϵ_2 and ϵ_3 give the energy position of the second and third maximum, respectively, in $\sigma_a(\epsilon)$; the first maximum is taken at ~ 0.0 eV.

^bSee Sec. III.F of Part I.

^cR. N. Compton, L. G. Christophorou, G. S. Hurst, and P. W. Reinhardt, J. Chem. Phys. 45, 4634 (1966).

^dC. Lifshitz, T. O. Tiernan, and B. M. Hughes, J. Chem. Phys. 59, 3182 (1973).

^eJ. P. Johnson, D. L. McCorkle, L. G. Christophorou, and J. G. Carter, J. Chem. Soc. Faraday Trans. 2 71, 1742 (1975); A. Hadjiantoniou, L. G. Christophorou, and J. G. Carter, J. Chem. Soc. Faraday Trans. 2 69, 1691 (1973); 69, 1704 (1973); P. M. Collins, L. G. Christophorou, and J. G. Carter, Oak Ridge National Laboratory Report ORNL/TM-2614, Oak Ridge, TN (1970).

^fP. W. Harland and J. C. J. Thynne, J. Phys. Chem. 75, 3517 (1971).

^gJ. C. J. Thynne, Dyn. Mass. Spectrom. 3, 67 (1972).

^hW. T. Naff, C. D. Cooper, and R. N. Compton, J. Chem. Phys. 49, 2784 (1968).

Further, we manipulated the multiple bonding (as in the series $2\text{-C}_2\text{F}_8$, $2\text{-C}_4\text{F}_8$, and $1,3\text{-C}_4\text{F}_8$) to investigate its influence on the magnitude and structure of the attachment cross section functions. Here, increase in multiple bonding rather than increase in size seems to increase $\sigma_a(\epsilon)$ both at thermal energies and at the ~ 0.2

eV peak. The cross sections for the triple bonded $2\text{-C}_4\text{F}_8$ and the twice double bonded $1,3\text{-C}_4\text{F}_8$ extend to slightly higher energies than the singly double-bonded $2\text{-C}_4\text{F}_8$. The position of the third NIR shifts to higher energies (see column 4 of Table V of Part I) with increasing multiple bonding.

TABLE VI. Thermal ($T=298^\circ\text{K}$) rates for electron attachment to $c\text{-C}_2\text{F}_8$, $c\text{-C}_6\text{F}_{10}$, $c\text{-C}_6\text{F}_{12}$, C_7F_8 , and C_8F_{16} .

Molecular formula	$(\alpha w)_{\text{meas.}}^a$ at $\langle \epsilon \rangle = 0.046$ eV ($10^8 \text{ sec}^{-1} \text{ torr}^{-1}$)	$(\alpha w)_{\text{ther., int.}}^b$ at $\langle \epsilon \rangle = 0.038$ eV ($10^8 \text{ sec}^{-1} \text{ torr}^{-1}$)	$(\alpha w)_{\text{ther., extr.}}^c$ at $\langle \epsilon \rangle = 0.038$ eV ($10^8 \text{ sec}^{-1} \text{ torr}^{-1}$)	$(\alpha w)_{\text{ther., lit.}}^d$ ($10^8 \text{ sec}^{-1} \text{ torr}^{-1}$)
$c\text{-C}_2\text{F}_8$	11.62	12.80	12.60	3.82
$c\text{-C}_6\text{F}_{10}$	11.00	10.02	12.85	10.14
$c\text{-C}_6\text{F}_{12}$	4.73	4.98	4.93	
C_7F_8	8.42	9.19	9.10	7.84
C_8F_{16}	2.49	2.40	2.40	

^aPresent work. Measured αw values in N_2 for $E/P=0.02 \text{ V cm}^{-1} \text{ torr}^{-1}$ ($\langle \epsilon \rangle = 0.046$ eV) at $T=298^\circ\text{K}$.

^bPresent work. Calculated thermal values from present $\alpha w(\epsilon)$ data (see Sec. III.E, Part I).

^cPresent work. Determined from two-point extrapolation of the $\alpha w(\epsilon)$ functions to $\langle \epsilon \rangle = 0.038$ eV.

^dF. J. Davis, R. N. Compton, and D. R. Nelson, J. Chem. Phys. 59, 2324 (1973).

TABLE VII. Direct current relative dielectric strengths for perfluorocarbons.

Compound		dc Relative dielectric strength ^{a,b}
SF ₆		1.0
c-C ₄ F ₈	(perfluorocyclobutane)	1.3–1.4
2-C ₄ F ₈	(perfluoro-2-butene)	1.7–1.8
1,3-C ₄ F ₆	(perfluoro-1,3-butadiene)	1.4
c-C ₄ F ₈	(perfluorocyclobutene)	1.7
2-C ₄ F ₆	(perfluoro-2-butyne)	2.2
c-C ₅ F ₈	(perfluorocyclopentene)	2.1–2.2
c-C ₆ F ₁₀	(perfluorocyclohexene)	1.9–2.2
c-C ₆ F ₁₂	(perfluoro-1,2-dimethylcyclobutane)	2.3–2.4
C ₇ F ₈	(perfluorotoluene)	~2.4
C ₈ F ₁₆	(perfluoro-1,3-dimethylcyclohexane)	~2.4

^aSphere-plane electrode geometry.^bFrom Refs. 2 and 4.

B. Relevance to gaseous dielectrics— the significance of negative ion resonances and electron attachment and the concept of multicomponent gaseous insulators

Over the past two decades, investigations of the interactions of slow electrons with molecules have led to the recognition of the importance of negative ion resonances in low-energy electron-molecule collisions. Not only are the numbers and the positions of such resonances strong functions of the molecular structure, but the magnitude of their respective cross sections can be very large compared to other "direct" scattering processes which can occur in electron-molecule collisions.

The NIR's can be efficient mechanisms for molecular rotational and vibrational excitation. They decay by electron emission and also, if energetically possible, by dissociative attachment; if the electron affinity of the molecule is positive and the excess energy removed, they can lead to stable parent negative ions. The NIR's are often described in terms of the molecular orbital(s) which the attached electron occupies.¹⁰

The NIR's play two important roles in improving the dielectric strength of gases which possess them.³ For those gases—such as N₂, H₂, etc.—which do not have positive electron affinities, NIR's are efficient mechanisms for removing energy from the electrons and thus inhibiting breakdown by an overall shift to lower energies of the electron energy distribution function in the gas under electrical stress.³ (The direct effect of these resonances on the dielectric strength of gases has been demonstrated.^{1–6}) For those compounds with positive electron affinities, such as the perfluorocarbons studied in this and the preceding paper, NIR's allow the efficient capture of electrons, especially at energies from 0.0 to ~1.5 eV. The extension of the electron attachment cross section to higher energies allows a larger overlap of the attachment cross section with the electron energy distribution function and consequently more efficient electron attachment at higher electrical stresses (see discussion in Refs. 1–6).

All of the perfluorinated hydrocarbons studied in this

and the preceding paper have been tested as gaseous dielectrics.^{1–6} In a direct comparison with sulfur hexafluoride (SF₆) under identical conditions (same electrode geometry, electrode separation, gas pressure, and temperature), they withstood between 1.4 and 2.4 times the dc voltage before breakdown as did SF₆ (see Table VII). These perfluorocarbon gases divide into two groups. In one group, the dielectric strength V_b is between 1.3 and 1.8 times that of SF₆. In the other group, V_b is between 2.1 and 2.4 times that of SF₆. The first group is comprised only of four-carbon containing compounds. These all have vapor pressures greater than 1 atm at room temperature and are good candidates as dielectric gases. In the second group, the molecules (with the exception of 2-C₄F₆) are more complex.

Although such increased complexity decreases vapor pressures—and practical applications require higher vapor pressures than those these compounds possess—they can be used in dielectric mixtures in combination with other gases.^{1–6} There seems to be no straightforward correlation between the structure of these compounds and their dielectric strength although the energy integrated attachment cross sections for the higher dielectric strength group are generally higher and both the attachment cross sections and dielectric strengths increase with increasing molecular complexity. (See Ref. 3 for a discussion of the effects of the microscopic molecular characteristics on V_b and Ref. 11 as to the significance of perfluorination.) The higher breakdown strength of 2-C₄F₆ compared to the other four-carbon containing compounds has been attributed^{1–6} to the extension of its $\sigma_a(\epsilon)$ to higher energies (see Fig. 8 of Part I) and to the presence of the triple bond which should affect (lower) the mean electron energy and shift the electron distribution to lower energies (see Refs. 2–4 and discussion later in this section).

The high dielectric strength of all ten perfluorocarbons studied in this paper and in Part I is large by virtue of their high $\sigma_a(\epsilon)$.^{1–5,11} As it has been discussed earlier^{1–5,11} and is elaborated upon below, indirect inelastic electron scattering via NIR's and large electron attachment cross sections over a wide energy range

above thermal energy crucially affect the breakdown strength of the dielectric.

In a gas discharge, the single most important parameter which determines the onset voltage of the discharge is the number density n_e of the free electrons in the gas. The rate of change of this quantity in a gas under an applied electric field is governed by the difference between the total ionization and the total electron attachment. These two quantities are related to the ionization cross section $\sigma_i(\epsilon)$, attachment cross section $\sigma_a(\epsilon)$, and the electron energy distribution function $f(\epsilon)$ by

$$\text{total ionization} \propto \int_I^\infty \sigma_i(\epsilon) f(\epsilon) d\epsilon, \quad (1)$$

$$\text{total attachment} \propto \int_0^\infty \sigma_a(\epsilon) f(\epsilon) d\epsilon, \quad (2)$$

where I is the ionization threshold energy. Given $\sigma_i(\epsilon)$ and $\sigma_a(\epsilon)$, $f(\epsilon)$ determines the values of net ionization (1) and net attachment (2). The distribution function is determined by the cross sections for elastic and inelastic electron scattering (especially through NIR states²⁻⁵) and to some extent by the attachment and ionization cross sections. Recently, we^{8,11} have obtained experimental evidence that the dielectric strength of a gas is more crucially affected by $\sigma_a(\epsilon)$ and the electron scattering cross sections determining $f(\epsilon)$, rather than by the ionization cross sections $\sigma_i(\epsilon)$.

Besides the present measurements on $\sigma_a(\epsilon)$ and some electron impact ionization cross section studies (see Refs. 5 and 11), no other cross section data exists on the interactions of slow electrons with the perfluorocarbons under consideration. For two of the perfluorocarbons studied—2-C₄F₈ and c-C₄F₈—the related "gross" quantities $\langle \alpha \rangle$ (mean ionization coefficient), $\langle \eta \rangle$ (mean attachment coefficient), w (electron drift velocity), and D_L/μ (ratio of lateral electron diffusion coefficient to electron mobility) have been measured by Naidu *et al.*¹² as a function of E/P in the range 90–210 and 140–270 V cm⁻¹ Torr⁻¹ for c-C₄F₈ and 2-C₄F₈, respectively.¹³ In these E/P ranges, the D_L/μ values for 2-C₄F₈ are lower than for c-C₄F₈. The smaller D_L/μ values are then reflected in the higher η 's and the lower α 's for 2-C₄F₈ over this E/P range through the fact that in Eqs. (1) and (2) a lower D_L/μ (i.e., a lower mean electron energy) implies a lower electron energy distribution $f(\epsilon)$ which would reduce Eq. (1) and increase Eq. (2) since $\sigma_i(\epsilon)$ is nonzero only above I and $\sigma_a(\epsilon)$ is highest at low energies.³ The $D_L/\mu(E/P)$ data of Naidu *et al.*¹² and the present $\sigma_a(\epsilon)$ measurements for c-C₄F₈ and 2-C₄F₈ could explain the superior V_b of 2-C₄F₈ over c-C₄F₈. Similar arguments could be advanced for the superior behavior of 2-C₄F₈ compared to the rest of the four-carbon containing perfluorocarbons in Table VII.

The previous^{1-6,11} and the present work underlines on the one hand the importance of effective electron scattering at low (subexcitation) energies to shift the electron energy distribution function to lower energies so that ionization is decreased and electron attachment is increased and, on the other hand, the importance of

large $\sigma_a(\epsilon)$ to high ϵ to allow maximum reduction in the electron density by optimizing the overlap of $\sigma_a(\epsilon)$ and $f(\epsilon)$.

Since a given molecule may not possess both large electron scattering and electron attachment cross sections over a wide energy range, it is unlikely that there is an optimum single gas as a dielectric. We have argued^{1-6,11} that it is in gas mixtures and on the basis of detailed knowledge on the magnitude and energy dependence of the slow electron-molecule collision processes that one would look to optimize both Eqs. (1) and (2). By introducing one or more component gases to shift $f(\epsilon)$ to low energies, where $\sigma_a(\epsilon)$ are the largest and one or more component gases to effect a $\sigma_a(\epsilon)$ as high as possible over as wide an energy range as possible, the dielectric capabilities of a gas mixture can be optimized.¹⁻⁶ A number of such mixtures with potential for practical application¹⁻⁶ and with superior properties to SF₆ have been developed in this manner (see Refs. 1–6 and 11).

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APPENDIX C

Field Detachment of an Electron from a Mononegative Ion

Harold C. Schweinler

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FIELD DETACHMENT OF AN ELECTRON FROM A MONONEGATIVE ION

Harold C. Schweinler

Earlier¹ we derived a formula for the transition probability per unit time of an electron from a singly charged atomic or molecular negative ion to the continuum under the influence of a uniform electric field. The formula which we obtained involved the probability, f_ℓ , that the electron in the most loosely bound state (in the absence of the field) be outside a sphere of radius r_0 . There f_ℓ was a specified parameter; here we introduce a simple model from which f_ℓ can be calculated. Furthermore, while the earlier model was applicable to bound excited states if they existed, we did not explicitly point this out. Accordingly, we shall extend our notations and formulas derived from our new model to bring this aspect of the problem to the fore.

In our new model we solve the Schrödinger equation

$$-(\hbar^2/2m)\nabla^2\psi_{\nu\ell m} + V(r)\psi_{\nu\ell m} = E_{\nu\ell} \psi_{\nu\ell m}$$

for the energy $E_{\nu\ell}$ and wave function $\psi_{\nu\ell m}(r, \theta, \phi)$ of the most loosely bound electron of the negative ion, taking for the potential energy $V(r)$ a "spherical square well":

$$V(r) = \begin{cases} -e\phi_i & 0 \leq r < r_0 \\ 0 & r_0 < r < \infty \end{cases}$$

That is, ϕ_i is the inner potential of the molecule. On making the usual substitution

$$\psi_{\nu\ell m}(r, \theta, \phi) = R_{\nu\ell}(r)Y_{\ell m}(\theta, \phi)$$

we obtain a differential equation for the radial amplitude $R_{\nu\ell}(r)$:

$$r^2 R_{\nu\ell}'' + 2r R_{\nu\ell}' + \left(\{2m[E_{\nu\ell} - V(r)]/\hbar^2\} r^2 - \ell(\ell+1) \right) R_{\nu\ell} = 0$$

Let $2m(E_{\nu\ell} + e\phi_i)/\hbar^2 = +K_{\nu\ell}^2$ and let $2mE_{\nu\ell}/\hbar^2 = -\kappa_{\nu\ell}^2$; then the well-behaved solution for $R_{\nu\ell}(r)$ is the spherical Bessel function $j_\ell(K_{\nu\ell}r)$ for $0 \leq r < r_0$ and the modified spherical Bessel function $k_\ell(\kappa_{\nu\ell}r)$ for $r_0 < r < \infty$. [In terms of solutions introduced earlier, $k_\ell(x) = i^{\ell+2} h_\ell^{(1)}(ix)$.] $j_\ell(x)$ and $k_\ell(x)$ for $0 \leq \ell \leq 5$ are given in Table I.

The solution which is continuous at $r = r_0$ is

$$R_{\nu\ell}(r) = \begin{cases} C_{\nu\ell} k_\ell(\kappa_{\nu\ell} r_0) j_\ell(K_{\nu\ell} r) & 0 \leq r \leq r_0 \\ C_{\nu\ell} j_\ell(K_{\nu\ell} r_0) k_\ell(\kappa_{\nu\ell} r) & r_0 \leq r \leq \infty \end{cases}$$

Continuity of radial derivative $R'_{\nu\ell}$ at $r = r_0$ gives after a little algebra

$$K_{\nu\ell} r_0 j_\ell'(K_{\nu\ell} r_0) / j_\ell(K_{\nu\ell} r_0) = \kappa_{\nu\ell} r_0 k_\ell'(\kappa_{\nu\ell} r_0) / k_\ell(\kappa_{\nu\ell} r_0)$$

This last equation gives the energy $E_{\nu\ell}$ in terms of the inner potential ϕ_i and the radius r_0 ; more explicitly, it is an implicit relationship between the two quantities $E_{\nu\ell} r_0^2$ and $e\phi_i r_0^2$, either one of which can thus be determined in terms of the other. We are preparing curves of $E_{\nu\ell} r_0^2$ as a function of $e\phi_i r_0^2$ and shall present them subsequently.

The coefficient $C_{\nu\ell}$ is obtained from the normalization condition

$$\int_0^\infty [R_{\nu\ell}(r)]^2 r^2 dr = 1 \quad :$$

$$C_{\nu\ell}^{-2} = [k_\ell(\kappa_{\nu\ell} r_0)]^2 \int_0^{r_0} [j_\ell(K_{\nu\ell} r)]^2 r^2 dr \\ + [j_\ell(K_{\nu\ell} r_0)]^2 \int_{r_0}^\infty [k_\ell(\kappa_{\nu\ell} r)]^2 r^2 dr.$$

The two integrals have the following values for $\ell > 0$

$$\int_0^{r_0} [j_\ell(K_{\nu\ell} r)]^2 r^2 dr = \frac{1}{2} r_0^3 \{ [j_\ell(K_{\nu\ell} r_0)]^2 - j_{\ell-1}(K_{\nu\ell} r_0) j_{\ell+1}(K_{\nu\ell} r_0) \}$$

$$\int_{r_0}^{\infty} [k_\ell(\kappa_{\nu\ell} r)]^2 r^2 dr = \frac{1}{2} r_0^3 \{ -[k_\ell(\kappa_{\nu\ell} r_0)]^2 + k_{\ell-1}(\kappa_{\nu\ell} r_0) k_{\ell+1}(\kappa_{\nu\ell} r_0) \}$$

For $\ell = 0$ their values are

$$\int_0^{r_0} [j_0(K_{\nu 0} r)]^2 r^2 dr = (2K_{\nu 0} r_0 - \sin 2K_{\nu 0} r_0)/4K_{\nu 0}^3$$

$$\int_{r_0}^{\infty} [k_0(\kappa_{\nu 0} r)]^2 r^2 dr = \exp(-2\kappa_{\nu 0} r_0)/2\kappa_{\nu 0}^3.$$

Our normalized exterior radial wave function was earlier taken to be $c_{0\ell} h_\ell^{(1)}(ikr) = i^{\ell+2} \kappa_{\nu\ell}^{3/2} f_\ell^{1/2} [N_\ell(\kappa_{\nu\ell} r_0)]^{-1} h_\ell^{(1)}(ikr)$. Our present form is $C_{\nu\ell} j_\ell(K_{\nu\ell} r_0) k_\ell(\kappa_{\nu\ell} r)$. Thus $\kappa_{\nu\ell}^3 f_\ell / [N_\ell(\kappa_{\nu\ell} r_0)]^2 = C_{\nu\ell}^2 [j_\ell(K_{\nu\ell} r_0)]^2$ or $f_\ell = [N_\ell(\kappa_{\nu\ell} r_0)]^2 [j_\ell(K_{\nu\ell} r_0)]^2 \div \kappa_{\nu\ell}^3 C_{\nu\ell}^{-2}$. Since $C_{\nu\ell}^{-2}$ contains a factor r_0^3 , we see that f_ℓ is a function of the variables $\kappa_{\nu\ell} r_0$ and $K_{\nu\ell} r_0$, which are themselves related by the transcendental equation which gives $E_{\nu\ell} r_0^2$ as a function of $e\Phi_i r_0^2$. In particular, $f_\ell / [N_\ell]^2$ is rigorously a function of $E_{\nu\ell} r_0^2$ on this model.

The final form which our equations take is then

$$\tilde{w}_{\nu\ell 0} = F_\ell(\tilde{E}_{\nu\ell} \tilde{r}_0^2) G(\tilde{E}_{\nu\ell}, \tilde{F})$$

$$F_\ell = (\ell + 1/2) [j_\ell(\tilde{K}_{\nu\ell} \tilde{r}_0)]^2 + \tilde{\kappa}_{\nu\ell}^3 C_{\nu\ell}^{-2}$$

$$G(\tilde{E}_{\nu\ell}, \tilde{F}) = [\tilde{F}/(-\tilde{E}_{\nu\ell})^{1/2}] \exp[-2(-\tilde{E}_{\nu\ell})^{3/2}/3\tilde{F}]$$

$$\tilde{w}_{\nu\ell 1} = [\ell(\ell + 1)/4] [\tilde{F}/(-\tilde{E}_{\nu\ell})^{3/2}] \tilde{w}_{\nu\ell 0}$$

F_ℓ is a slowly varying function except for very loosely bound electrons. Thus the analysis would proceed as follows: (a) Plot the natural logarithm of $\tilde{W}(-\tilde{E})^{1/2}/\tilde{F}$ against $1/\tilde{F}$, and determine the slope at moderately low values of $\tilde{F}$. The slope gives $-\tilde{E}$. (b) On the curve of $\tilde{E}\tilde{r}_0^2$ versus $\tilde{\phi}_i\tilde{r}_0^2$ plot the straight lines $\tilde{E}/\tilde{\phi}_i = S$ for several values of ϕ_i (... , 6 volts, 8 volts, 10 volts, ...). The intersections of these curves will give $\tilde{r}_0$. If there are more than one value of $\tilde{r}_0$ determined in this way, requirements of physical reasonableness placed (from experience) on ϕ_i and r_0 may suggest whether the bound state is the ground state of an excited state, and even suggest the degree of excitation (ν).

Table I. $j_\ell(x)$ and $k_\ell(x)$

ℓ	$j_\ell(x)$
0	$(1/x)\sin x$
1	$(1/x^2)\sin x - (1/x)\cos x$
2	$(3/x^3 - 1/x)\sin x - (3/x^2)\cos x$
3	$(15/x^4 - 6/x^2)\sin x - (15/x^3 - 1/x)\cos x$
4	$(105/x^5 - 45/x^3 + 1/x)\sin x - (105/x^4 - 10/x^2)\cos x$
5	$(945/x^6 - 420/x^4 + 15/x^2)\sin x - (945/x^5 - 105/x^3 + 1/x)\cos x$
ℓ	$k_\ell(x)$
0	$\exp(-x)(1/x)$
1	$\exp(-x)(1/x + 1/x^2)$
2	$\exp(-x)(1/x + 3/x^2 + 3/x^3)$
3	$\exp(-x)(1/x + 6/x^2 + 15/x^3 + 15/x^4)$
4	$\exp(-x)(1/x + 10/x^2 + 45/x^3 + 105/x^4 + 105/x^5)$
5	$\exp(-x)(1/x + 15/x^2 + 105/x^3 + 420/x^4 + 945/x^5 + 945/x^6)$

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APPENDIX D

Toxicity of Perfluoro-butene-2

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NUCLEAR DIVISION*INTERNAL CORRESPONDENCE*

March 20, 1979

TO: Dr. L. G. Christophorou
Health and Safety Research Division

FROM: M. E. Boling
Biology Division

The acute inhalation toxicity experiment performed on June 15, 1978 and reported on June 30, 1978 was repeated on March 14, 1979 using all the same conditions except that the mixture of air and perfluoro-butene-2 was cooled in a glass chamber immersed in an anti-freeze solution at -15°C before entering the inhalation chamber. The temperature in the chamber was 23°C throughout the exposure. The total exposure time was 22.5 hours. The flow rates were 12 liters/min for air and 12 ml/min for the perfluoro-butene-2, giving a nominal ratio of 1000 ppm.

The results were the same as on June 15, 1978. The mice were weak and dyspneic at the time of termination of exposure and were all dead within four days.

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