DIELECTRIC STRENGTHS OF NEW GASES AND GAS MIXTURES*

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ABSTRACT

We have argued earlier and we emphasize further in this paper that the most effective gaseous dielectrics are gas mixtures with components chosen on the basis of fundamental physicochemical knowledge, especially on low-energy electron-molecule interactions. On the basis of such knowledge, especially on electron attachment and electron slowing down, a number of new gases and gas mixtures have been found with breakdown strengths superior to pure SF_6. These include the unitary gases c-C_4F_8 (perfluorocyclobutane), C_4F_8 (perfluorobutene-2), C_4F_6 (perfluoro-2-butyne), C_6F_{10} (perfluorocyclohexene), C_5F_8 (perfluorocyclopentene), and C_6F_{12} (perfluorodimethylcyclobutane), and the multicomponent gas mixtures 20% C_4F_6 + 80% SF_6, 40% C_4F_6 + 60% N_2, 50% C_4F_6 + 50% SF_6, and 30% C_4F_6 + 20% SF_6 + 50% N_2 with DC breakdown strengths relative to SF_6 of 1 equal to 1.4, 1.8, 2.2, 2.1, 2.2, 2.4, 1.3, 1.4, 1.75, and 1.33, respectively. Our findings on these and other systems will be presented and discussed. Results will be presented and discussed, also, on the dielectric strengths of some of the above new gases measured with cylindrical electrode geometries using different center conductor diameters. Finally, our findings on the initial decomposition products of some of the new insulators caused by electron impact will be presented and their implications assessed.

INTRODUCTION

As electric transmission line voltage levels continue to increase, there is a corresponding need to upgrade the performance of gaseous dielectrics. Existing gaseous insulators clearly do not meet all of

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the requirements of the power industry, and it is unlikely that any single gas will be satisfactory for all conditions. Solutions, therefore, to the many and varied problems and needs relating to high voltage insulation (and improvements over present procedures) must be sought in the development and use of multicomponent gas mixtures.

We anticipate that the best multicomponent gaseous insulators will be comprised of components selected according to basic knowledge on their physical and chemical properties. Especially significant among these are the basic processes involved in the interaction of low-energy electrons with the dielectric gas molecules, such as electron attachment, electron energy loss, and electron impact ionization, as a function of electron energy and the relation of these to molecular structure.

We have undertaken a systematic investigation of the basic and applied aspects of the dielectric strengths of unitary and multicomponent gaseous systems, and in this paper we present and briefly discuss some of the pertinent findings of this work.

APPARATUS

Two pieces of apparatus have been employed in the present investigations of breakdown voltages of gases and gas mixtures. The first apparatus consisted of a small stainless steel chamber approximately 6 liters in volume which could be evacuated to less than 10^{-6} torr. The high voltage electrode was a 3/4-in. stainless steel sphere and the ground electrode was a 3-1/2-in. stainless steel plane mounted onto a micrometer drive. Negative high voltage was applied to the sphere by a 60-kV power supply. The electrode separation was kept small to approximate uniform field conditions (e.g., a 1-mm electrode gap resulted in a field nonuniformity of $\sim$3.5%).

The second apparatus comprised a larger chamber of $\sim$40 liters volume which was routinely evacuated to less than 10^{-6} torr before gas was admitted to the chamber. The electrode assembly consisted of two stainless steel planes, the profiles of which were designed according to the work of Pearson and Harrison.[1] A 300-kV DC power supply (Deltatron L300-2C) from Delta Ray Corporation provided a negative high voltage relative to the grounded electrode.

Both apparatuses had similar controllers which automatically ramped the voltage, detected the spark, and held the breakdown voltage reading on a digital voltmeter. Ultraviolet light from a deuterium lamp was used to irradiate the electrodes. To obtain a data point, usually a minimum of ten breakdowns were recorded at each value of P and d (P is the gas pressure and d is the electrode separation), and the average value and standard deviation were calculated. The ratio of the standard deviation to the mean was used as a measure of the scatter in the data. In general this scatter was $\lesssim$2% for the sphere-plane geometry, although at the highest values of Pd employed, this scatter was at times larger (still, however, <5%). With the plane-plane electrode geometry the scatter was $\lesssim$1% below 200 kV and typically between 2 to 3% above $\sim$200 kV.

BREAKDOWN STRENGTHS - UNITARY GASES

Dielectric Gases with Vapor Pressures in Excess of One Atmosphere

In our investigations we have found a number of high vapor pressure (>1 atm at ambient temperature) gases which have high dielectric strengths. Some of these gases, their dielectric strengths relative to that of SF_6, and their vapor pressures at ambient temperatures are listed in Table 1. In Fig. 1 are shown the breakdown voltages, V_s, for a number of unitary gases as functions of Pd. The fluorocarbons were found to have the highest dielectric strength; C_4F_6 (perfluoro-2-butyne) in particular has more than twice the dielectric strength of SF_6. The double-bonded C_4F_8 (perfluorocyclobutene-2) and the cyclic-C_4F_8 (perfluorocyclobutane) compounds are two other fluorocarbons with high dielectric strengths. Perfluoropropane (C_3F_8), although with eight fluorine atoms, has a dielectric strength slightly lower than SF_6. This molecule, however, has no double bonds and attaches low-energy electrons very weakly.[3]

The breakdown voltage, V_s, in uniform electric fields was found to be a function of Pd and not an explicit function of P alone. A possible exception, however, seems to be SF_6 which for pressures >2000 torr shows[4] deviation from Paschen's law.

Table 1. Relative DC Breakdown Strengths of Some Unitary Gases (Vapor Pressures ≥1 Atm)[a]

Gas	Relative Strength	Vapor Pressure Atm (°C)
C_4F_6 (perfluoro-2-butyne)	2.2	≥4.8[b] (23)
C_4F_8 (perfluorobutene-2)	1.7-1.8	2.02[c] (21.1)
c-C_4F_6 (perfluorocyclobutene)	1.7	>1[d]
C_4F_6 (perfluoro-1,3-butadiene)	1.4	>1[e]
c-C_4F_8 (perfluorocyclobutane)	1.3-1.4	2.9[f] (24.3)
SF_6 (sulfur hexafluoride)	1.0	22.77[c] (21.1)
C_3F_8 (perfluoropropane)	0.93	7.81[c] (21.1)
N_2 (nitrogen)	0.40	g
CO_2 (carbon dioxide)	0.37	57.5[c] (21.1)

[a]All breakdown strength data are from Ref. 4 except those on c-C_4F_6 which are unpublished recent results by the Oak Ridge group.

[b]Present estimated value.

[c]William Braker and Allen L. Mossman, Matheson Gas Data Book, 5th Ed., Matheson Gas Products, East Rutherford, New Jersey, 1971.

[d]Boiling point = 7.4-7.6°C.

[e]Boiling point = 5-6°C.

[f]E. C. Coyner and D. Hanesian, Freon Technical Bulletin EL-5, E. I. du Pont de Nemours and Company, Inc., 1964.

[g]Critical temperature -147.1°C; N_2 cannot be liquefied at temperatures higher than this.

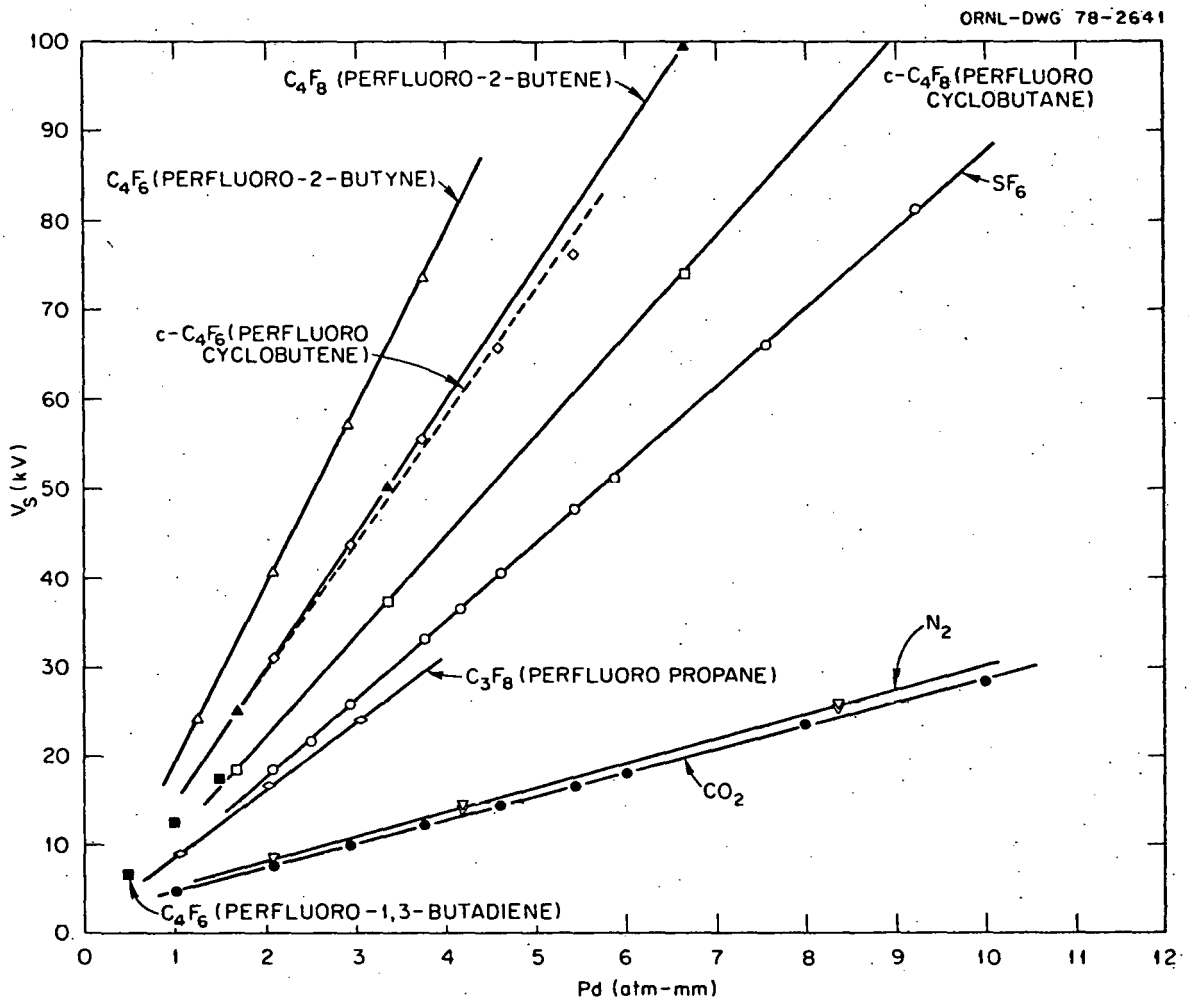

Fig. 1. Breakdown voltage, V_S, as a function of Pd for high pressure ($\gtrsim$1 atm) unitary gases. The CO_2 data are from Ref. 2.

Dielectric Gases with Vapor Pressures Less Than One Atmosphere

Many compounds with vapor pressures less than one atmosphere at room temperature were found to have higher dielectric strengths than SF_6 at comparable pressures. The relative breakdown strengths of some of these are given in Table 2, and the V_S vs Pd curves are shown in Fig. 2. The pressures employed ranged from 20 torr for C_7F_8 (octafluorotoluene) to 281 torr for C_4F_6 (hexafluoro-1,3-butadiene). Comparisons with SF_6 were made only when SF_6 could be measured at the same or nearly the same pressure. The curvature of the breakdown voltage vs Pd seen in Fig. 2 is due to the low pressures employed which required the electrode

Table 2. Relative DC Breakdown Strengths of Some Low Vapor Pressure Compounds[a]

Compound	Relative Strength
C_6F_{12} (mixture of 1,2- and 1,3-perfluorodimethylcyclobutane)[b]	2.3-2.4
C_5F_8 (perfluorocyclopentene)[c]	2.1-2.2
C_6F_{10} (perfluorocyclohexene)	1.9-2.2
C_7F_{14} (perfluoromethylcyclohexane)[d]	2.1
C_8F_{16} (perfluoro-1,3-dimethylcyclohexane)	$\sim$2.3[e]
C_7F_8 (octafluorotoluene)	$\sim$2[f]
C_7F_{14} (perfluoroheptene-1)	1.2
SF_6 (sulfur hexafluoride)	1.0

[a]Data from Ref. 4 except as noted.

[b]At 26.7°C the vapor pressure is 394.3 torr.

[c]Boiling point = 25°C.

[d]At 21.7°C the vapor pressure is $\sim$95 torr.

[e]At low pressures the V_s for this compound was found to be 1.3 times that of C_4F_6 under identical experimental conditions.

[f]Unpublished result of the Oak Ridge group, measured with respect to C_8F_{16} under identical experimental conditions.

separation to be relatively large (up to 10 mm in some cases) in order to obtain Pd values in the range $0.5 \lesssim Pd \lesssim 2.5$ atm-mm. Hence, the electric field was highly nonuniform in these cases, and in general the breakdown voltage was not a linear function of Pd.

These low vapor pressure compounds, although unsuitable by themselves as dielectrics due to their low vapor pressures at room temperature, may

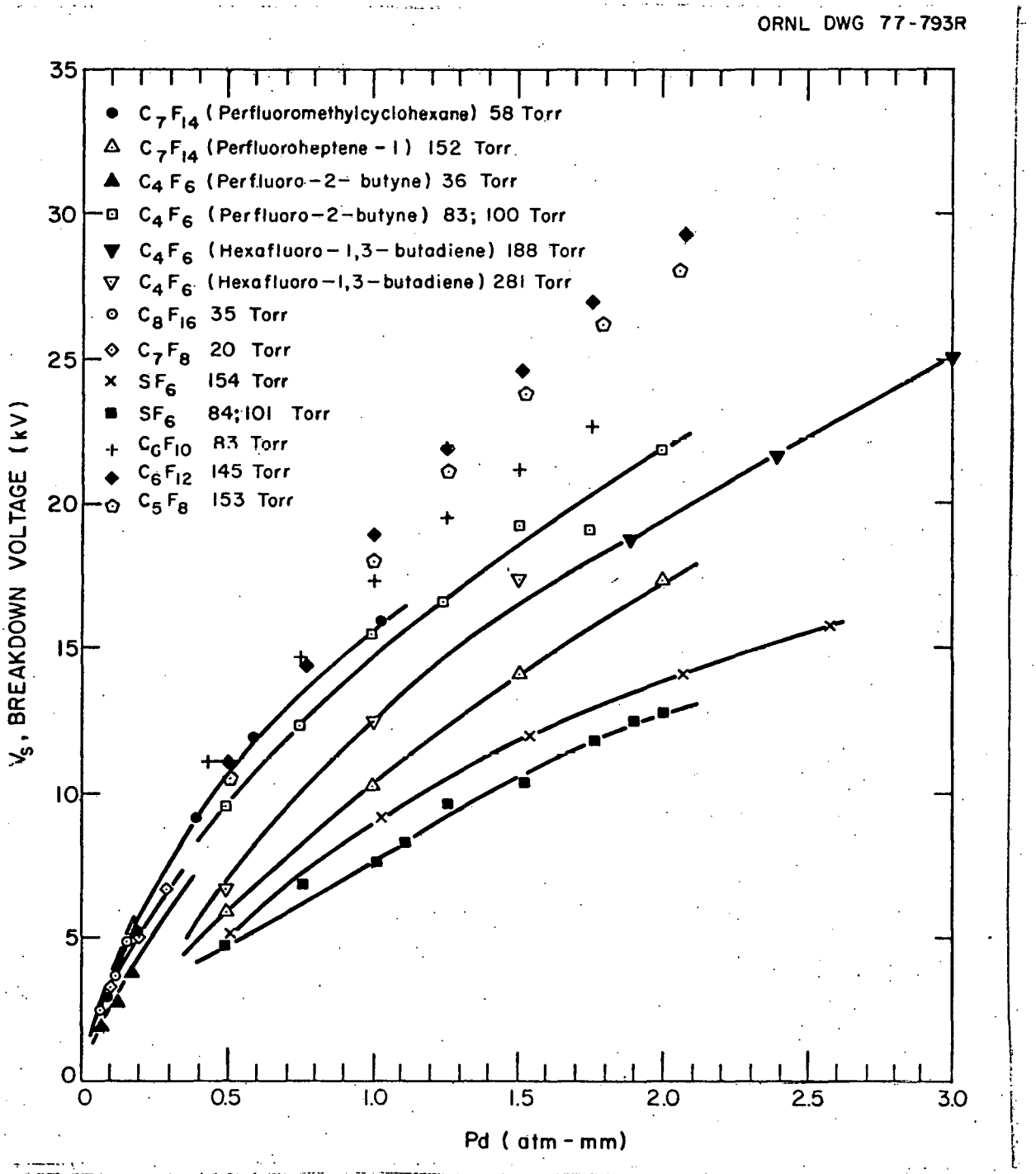

Fig. 2. Breakdown voltage, V_S, as a function of Pd for low pressure (<1 atm) unitary gases at the indicated pressures for sphere-plane electrode geometry.

have potential use as additives to higher pressure buffer gases such as N_2. For example, a 10% C_6F_{10}/90% N_2 mixture at 500 torr total pressure has a 20% higher breakdown voltage than a 10% SF_6/90% N_2 mixture at the same pressure. But, even more importantly, the study of these gases provides basic information necessary for the understanding of the role of fundamental physical processes in the electrical breakdown.

The Role of Electron Attachment as a Function of Electron Energy

In order to develop new improved gas dielectrics, the basic physical properties of the dielectric itself must be identified and understood, especially in relation to their effect on the breakdown voltage. We have been investigating the role of one such basic property of the dielectric; namely, electron attachment as a function of electron energy. Although our systematic study of the electron attachment properties of the compounds in Tables 1 and 2 is still not complete, the data presented in Fig. 3 are quite revealing.

Let us, then, draw our attention to Fig. 3 where the electron attachment cross section as a function of electron energy, $\sigma_a(\varepsilon)$, is plotted for several gases of high dielectric strength.[4-6] The line designated as $\pi\lambda\!\!\!^{-2}$ represents the maximum s-wave capture cross section ($\lambda\!\!\!^{-} = \lambda/2\pi$ and λ is the electron deBroglie wavelength). The $\sigma_a(\varepsilon)$ for SF_6 approaches the theoretical maximum at near-thermal energies and is quite large at $\sim$0.3 eV. (The peak at $\sim$0.3 eV is due to SF_5^- while at thermal energies SF_6^- is the dominant ion formed.) At energies $\gtrsim$0.4 eV, the SF_6 capture cross section rapidly decreases so that SF_6 cannot effectively capture electrons with kinetic energies in excess of this energy. It is seen from Fig. 3 that the attachment cross sections for c-C_4F_8, C_4F_8, and C_4F_6 remain substantial to electron energies $\gtrsim$1 eV. These latter gases, therefore, are capable of capturing effectively electrons to much higher energies than SF_6. Our breakdown measurements (Table 1) clearly show that for the latter group of compounds the breakdown strengths are significantly higher than that of SF_6. On the basis of these findings and additional measurements currently in progress,[6]

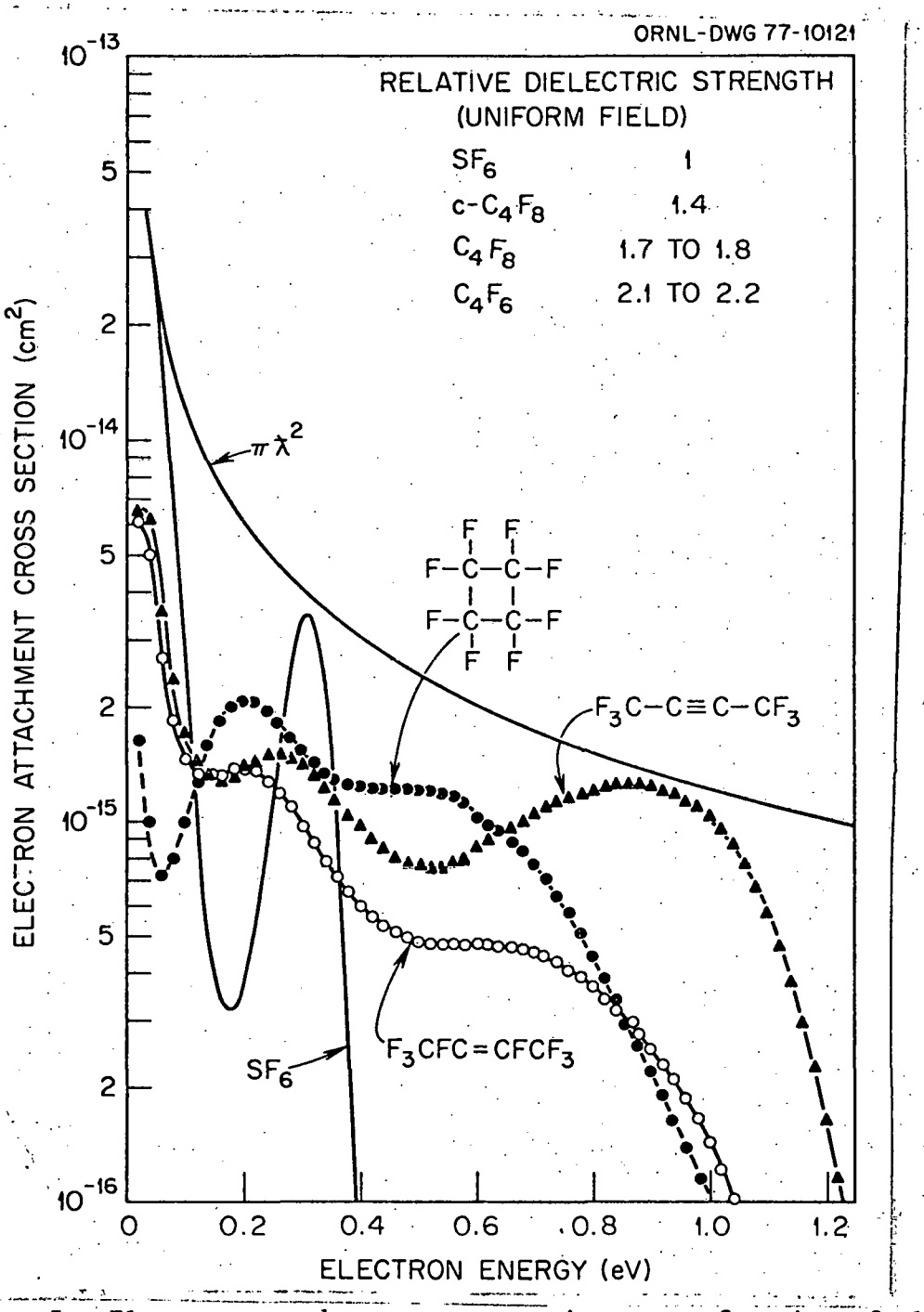

Fig. 3. Electron attachment cross sections as a function of electron energy for SF_6, c-C_4F_8, C_4F_8 (perfluorobutene-2), and C_4F_6 (perfluoro-2-butyne). $\pi\lambda^2$ is the maximum s-wave electron capture cross section (Refs. 5 and 6).

the efficient capture of electrons in the range of energies $0.4 \leq \varepsilon \leq 1.2$ eV evidently reduces significantly the number of free electrons available for initiating breakdown, with a resultant increase in the breakdown strength of the dielectric. More generally, the overlap of the electron energy (or velocity) distribution with the electron attachment cross section must be sufficiently large to cause a substantial increase in the breakdown voltage.

Optimizing the Gaseous Dielectric

We have suggested earlier[5] the criteria for an optimum gas dielectric; namely, that a good dielectric should maximize the quantity

$$\int_0^\infty \sigma_a(\varepsilon) f(\varepsilon, E/P) d\varepsilon \qquad \text{[maximize]} \tag{1}$$

and minimize the quantity

$$\int_I^\infty \sigma_i(\varepsilon) f(\varepsilon, E/P) d\varepsilon \qquad \text{[minimize]}, \tag{2}$$

where $\sigma_a(\varepsilon)$ and $\sigma_i(\varepsilon)$ are the electron-attachment and electron-impact ionization cross sections, respectively, and $f(\varepsilon, E/P)$ is the electron energy distribution function as a function of electron energy ε and pressure reduced electric field E/P, and I is the ionization threshold energy.

Condition (1) is satisfied when $\sigma_a(\varepsilon)$ is as large as possible over as wide an energy range as possible. Since electron attachment processes are resonant processes with cross sections decreasing with increasing energy position of the resonance (see Fig. 3 and Ref. 5), $f(\varepsilon, E/P)$ should be shifted to as low an energy as possible. To fulfill condition (2), the ionization threshold would need to be high and the energy distribution shifted to low energies. Thus in each case the electron energies should be reduced as much as possible. Such a reduction in the electron energy is accomplished by elastic and especially

inelastic electron scattering processes, some of which are discussed in the next section on dielectric mixtures.

Important as the electron energy distribution function is in assessing the role of the various basic processes on breakdown [see relations (1) and (2)], to our knowledge presently there are no direct measurements of this quantity for gaseous media under prebreakdown conditions. There exists only a limited indirect knowledge of $f(\varepsilon,E/P)$ for some simple gases. The main difficulty in computing $f(\varepsilon,E/P)$ from electron transport data lies in the fact that a large amount of basic detailed information on the microscopic cross sections is required, which for a complex molecular gas or a gas mixture makes the indirect deduction of $f(\varepsilon,E/P)$ very uncertain. Plans to measure directly $f(\varepsilon,E/P)$ for pure polyatomic gases and gas mixtures under prebreakdown conditions are under consideration at our laboratory.

Prior to closing this section, it is emphasized that important as the process of electron attachment is in affecting the dielectric strength of a gaseous medium, it is not the only gas property which determines the behavior of the gaseous dielectric. Elastic and inelastic (especially indirect via negative ion resonances[5]) electron scattering as well as electron impact ionization at low energies can also be crucial [see relations (1) and (2)]. It can be seen, for example, from Fig. 3 that the electron attachment cross section above thermal energies for c-C_4F_8 is generally higher than that for C_4F_8 (perfluorobutene-2), although the breakdown voltage of c-C_4F_8 is substantially less than that of its isomer. This may be due to the presence of the double bond in perfluorobutene-2, since, as we have shown earlier for a number of hydrocarbons,[3] the presence of double and triple bonds lowers the average electron energy at a given E/P.

Basic studies at our laboratory have been and are being aimed at the identification of the mechanisms of electron energy loss and on the dependence of the cross sections of these on the details of the molecular structure. It is on the basis of such knowledge that we would hope to optimize our choice of dielectric gases.

BREAKDOWN STRENGTHS - GAS MIXTURES

Gas mixtures as dielectrics have the advantage that they can be tailored to a specific need, whereas a unitary gas must be universally good under all conditions. For example, SF_6 performs well in uniform fields, but in the presence of nonuniform fields (as in the case of particle contamination) its strength deteriorates considerably. It is quite possible that gas mixtures can have a greatly improved nonuniform field performance.

There are several ways to approach systematically the development of dielectric gas mixtures, all of which require detailed knowledge of basic cross sections in order to assess the compatibility of the component gases and to maximize synergistic effects. One approach involves the use of several electron attaching gases in combination to map as wide an energy range as possible with large electron attachment cross sections. In this manner, one attempts to approach the theoretical maximum electron attachment cross section (see Fig. 3) and hence maximize expression (1). As far as electron attachment is concerned, this would be the optimal dielectric. Another approach involves the use of efficient electron attaching and electron slowing down gases, the latter being used for the purpose of shifting $f(\varepsilon,E/P)$ to lower energy and in such a way as to optimize (1) and (2).

Binary Mixtures of Efficient Electron Attaching Gases

In Table 3 data are presented on the relative breakdown strengths of binary mixtures of C_4F_6 and SF_6. The relative breakdown strength of the binary mixture increases with the amount of C_4F_6. The measured relative strengths were in each case larger than the weighted average (fraction of C_4F_6 x relative strength of C_4F_6 + fraction of SF_6 x relative strength of SF_6) calculated by using a relative breakdown strength of 2.2 for C_4F_6. These results indicate a synergistic effect between the two gases.

Table 3. Relative Breakdown Strengths of Binary Mixtures of SF_6 and C_4F_6 (perfluoro-2-butyne) ($T = 298°K$, $P_{total} = 500$ torr)

Percentage of Mixture		Measured Relative Breakdown Strength	Weighted Average[a]
C_4F_6	SF_6		
5	95	1.10	1.06
10	90	1.17	1.12
20	80	1.30	1.24
50	50	1.75	1.60
0	100	1.00	1.00

[a]See text.

From the discussion given earlier in this section, synergism in the dielectric behavior of a gas mixture must be traced to the details of the interaction of free electrons with the gas molecules comprising the mixture and the magnitudes and energy dependences of the associated cross sections. If the component gases interact with electrons in different energy ranges and with large cross sections, then—depending on the magnitude and energy dependence of their cross sections—they may cooperate in ameliorating the effects of free electrons, especially if the cross sections of each are small outside of a narrow energy range. Sulfur hexafluoride (SF_6) with an attachment cross section $\sigma_a(\varepsilon)$ confined mostly to thermal energies would be expected to show a great degree of synergism as an additive with other gases. This is borne out by the data in Tables 3 and 4.

Figure 4 shows the breakdown voltage of a 20% C_4F_6/80% SF_6 mixture at a high ($\sim$4.7 atm) total pressure. The relative improvement over pure SF_6 is the same as for the low pressure mixture in Table 3.

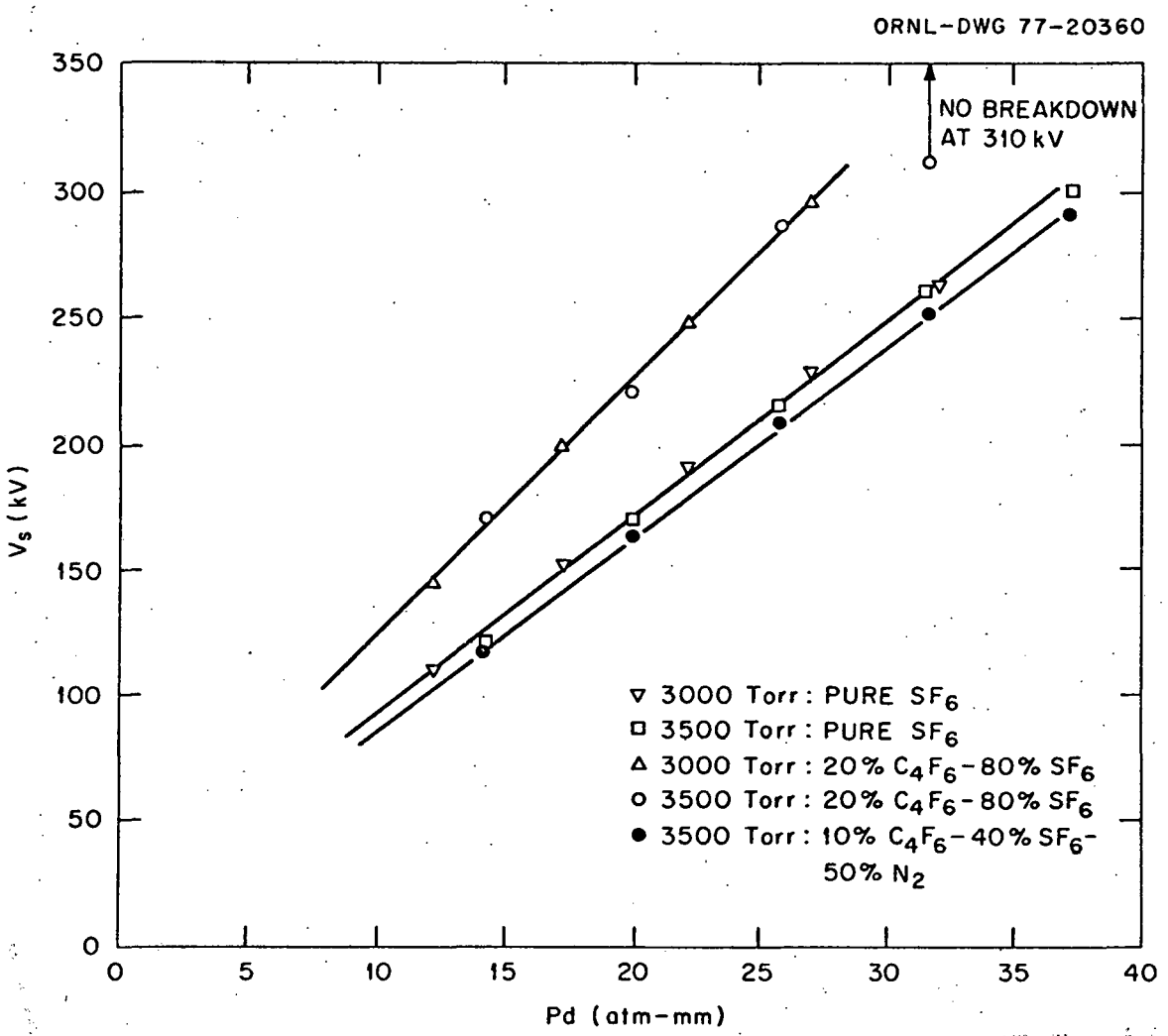

Fig. 4. Breakdown voltage, V_s, for pure SF_6 and for SF_6/C_4F_6 (perfluoro-2-butyne) and $SF_6/C_4F_6/N_2$ mixtures as a function of Pd for pressures 3000 to 3500 torr (sphere-sphere electrode geometry).

Binary Mixtures of Efficient Electron Attaching and Electron Slowing Down Gases

Although basic physicochemical knowledge does not yet permit a quantitative prediction of the breakdown strength and other dielectric properties of a gas, the available basic knowledge can be used as a guide for a systematic study of mixtures. An investigation of the breakdown voltages for several electron attaching gas mixtures using N_2 as the electron slowing down agent or buffer gas was made, and the results appear in Fig. 5. The Pd value was held constant at 4.6 atm-mm. By

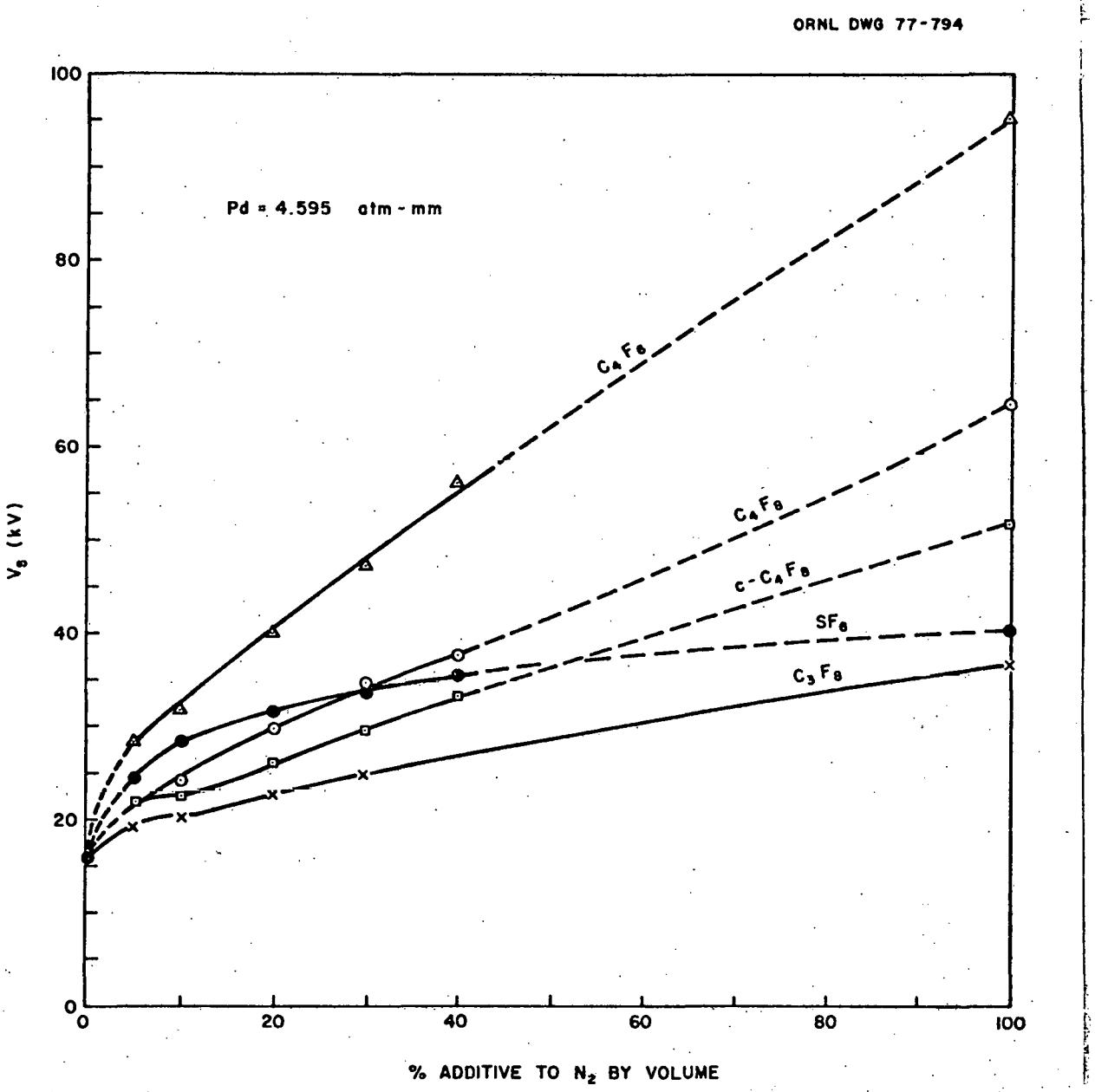

Fig. 5. Breakdown voltages, V_S, vs percent of electron attaching additive to N_2 by volume (plane-plane electrode geometry).

measuring the breakdown voltage as a function of the percentage of the electron attaching gas, we can compare the synergistic effect of each in combination with N_2.

For all five gases (SF_6, C_4F_6, C_3F_8, C_4F_8, and c-C_4F_8) the corresponding binary mixtures with N_2 show synergism. As expected from the electron attachment cross sections (Fig. 3), the mixtures with SF_6

show the largest synergism. A mixture of 40% SF_6/60% N_2 realizes 80% of the dielectric strength of pure SF_6. The rest of the electron attaching gases show a sharp increase in V_s at low percentage mixtures, but subsequently V_s increases essentially linearly with concentration showing no evidence of the saturation effect evident in the SF_6/N_2 mixtures.

Carbon dioxide (CO_2) also exhibits synergism when combined with electron attaching gases. In Table 4, the breakdown voltage is shown for mixtures of 20% of an efficient electron attaching gas and 80% CO_2, or 40% CO_2 + 40% N_2, or 80% N_2. It is clearly seen that CO_2 is slightly better than N_2 as a buffer gas for c-C_4F_8. A slight synergism between CO_2 and N_2 is also discernable for the C_4F_8 containing mixtures. These synergistic effects must relate to the electron slowing down properties of CO_2.[5,7]

Synergism in Multicomponent Gas Mixtures

Cooperative effects arising from proper combinations of electron attaching and electron slowing down gases can be seen from the data in Table 5, where the dielectric strengths of mixtures (see Ref. 4 for a complete list of these) comprising the gases N_2, SF_6, C_4F_6, and C_3F_8 are listed. Two of the salient features of these data are: (1) C_4F_6, as is expected from its dielectric strength in the pure form, is very effective as an additive. Thus entries 11 and 12 with the highest percentage of C_4F_6 have the highest breakdown voltage. (2) C_3F_8 by itself or in mixtures with only N_2 (entries 2 and 6) is not particularly effective. When, however, C_3F_8 is used in combination with N_2, C_4F_6, and SF_6—as in entries 9 and 10, 11 and 12, and 13 and 14—it is more effective than an equal amount of SF_6.

Effect of Indirect Electron Scattering Via Negative Ion Resonances on the Dielectric Strength of Binary Mixtures

The significance of negative ion resonances (NIRs) in slowing down subionization and especially subexcitation electrons has been discussed earlier.[5] A number of studies have shown that for many substances (see,

Table 4. Mixtures of Effective Electron Attaching Gases with CO_2
(T = 298°K, P $\sim$ 0.66 atm, Pd = 4.6 atm-mm)

Mixture	Breakdown Voltage[a,b] (kV)	Weighted Average (kV)
20% c-C_4F_8/80% N_2	25.0	23.1
20% c-C_4F_8/40% CO_2/40% N_2	25.7	22.2
20% c-C_4F_8/80% CO_2	26.0	21.3
20% C_4F_8/80% N_2	28.7	26.3
20% C_4F_8/40% CO_2/40% N_2	28.9	25.4
20% C_4F_8/80% CO_2	28.5	24.5
20% C_4F_6/80% N_2	40.1	31.3
20% C_4F_6/40% CO_2/40% N_2	39.1	30.4
20% C_4F_6/80% CO_2	38.1	29.5
20% C_3F_8/80% N_2	22.8	20.1
20% C_3F_8/40% CO_2/40% N_2	22.4	19.2
20% C_3F_8/80% CO_2	20.8	18.3
20% SF_6/80% N_2	30.1	20.7
20% SF_6/40% CO_2/40% N_2	28.7	19.8

[a]The uncertainty is less than 0.1 kV.

[b]These breakdown voltages are averages of ten breakdown measurements taken with plane-plane electrode geometry and 0.275-in. electrode gap.

for example, Refs. 8 and 9) electron scattering (elastic and inelastic) at low energies proceeds predominantly through such states. These electron-molecule (negative ion) states are formed[7,8,10] when slow electrons interact with molecules and are nonstationary (i.e., they decay, often

Table 5. Dielectric Strengths of Unitary, Binary, and Multicomponent Mixtures of N_2, SF_6, C_4F_6, and C_3F_8 ($T = 298°K$, $P \sim 0.66$ atm)[a]

Percent Component					V_s (kV)
No.	N_2	SF_6	C_4F_6	C_3F_8	
1	—	100	—	—	40.4
2	—	—	100	—	93.5
3	—	—	—	100	36.4
4	80	20	—	—	30.1
5	80	—	20	—	40.1
6	80	—	—	20	22.8
7	80	10	10	—	36.0
8	80	10	—	10	29.8
9	60	20	20	—	43.2
10	60	10	20	10	47.7
11	50	20	30	—	53.7
12	50	10	30	10	55.4
13	50	20	20	10	47.0
14	50	10	20	20	48.3

[a]Average of ten independent measurements at a Pd value of 4.6 atm-mm (plane-plane electrode geometry).

in as short a time as $\sim 10^{-16}$ sec). Upon decay, the neutral molecule can retain part or all of the impacting electron's energy, the electron being slowed down in the process.

We have investigated the use of systems possessing such NIRs as "electron slowing down" gases in mixtures with one or more highly

electron attaching gases. The electron slowing down gases we used do not normally attach electrons themselves but act to lower the energy of the free electrons so that the electron attaching additive(s) can efficiently remove them in the form of negative ions.

Figure 6 shows the cross sections for vibrational excitation via NIR for CO, N_2, and H_2 as a function of electron energy. These gases were used since basic data for them already exist. Additional basic data are needed. For CO and N_2 the cross sections are the sums of the first eight vibrational levels[11]; for H_2 the cross section for only the first vibrational level is given since the higher ones are very much lower in magnitude. The H_2 cross section has been multiplied by 1.4 to correct for anisotropic scattering.[7] The magnitude of the cross sections decrease in the order CO > N_2 > H_2. One would expect on the basis of the NIR cross section data alone that the breakdown voltage should decrease in the order CO > N_2 > H_2. This is clearly seen from the uniform-field measurements on V_s presented in Table 6. V_s decreases in the order CO > N_2 > H_2. Since the electron attachment cross sections for these systems are exceedingly small or zero,[7] the differences in their dielectric strength is attributed to their relative effectiveness in slowing down electrons via their respective NIRs. Similar conclusions can be drawn from the results on binary mixtures of C_4F_6 and SF_6 each with H_2, N_2, and CO presented in Table 6.

BREAKDOWN STRENGTHS OF GASES/MIXTURES WITH CYLINDRICAL ELECTRODES

In Fig. 7 a and b, preliminary data[4] are presented on the breakdown voltages of mixtures of SF_6 and c-C_4F_8 each with N_2 obtained using cylindrical electrodes comprising an inner stainless steel electrode of 0.4 cm radius inside an outer cylinder of inner radius of 2 cm. The total pressure was 760 torr (1 atm), and the SF_6/N_2 and c-C_4F_8/N_2 concentration fraction was varied from 0 to 100% by pressure. The outer cylinder was at ground potential, and the inner cylinder was at either polarity of high voltage. Each data point is the average of at least ten breakdowns and for each the random scatter (standard deviation ÷ mean) was less than 3%. The uniform field breakdown strength data shown in

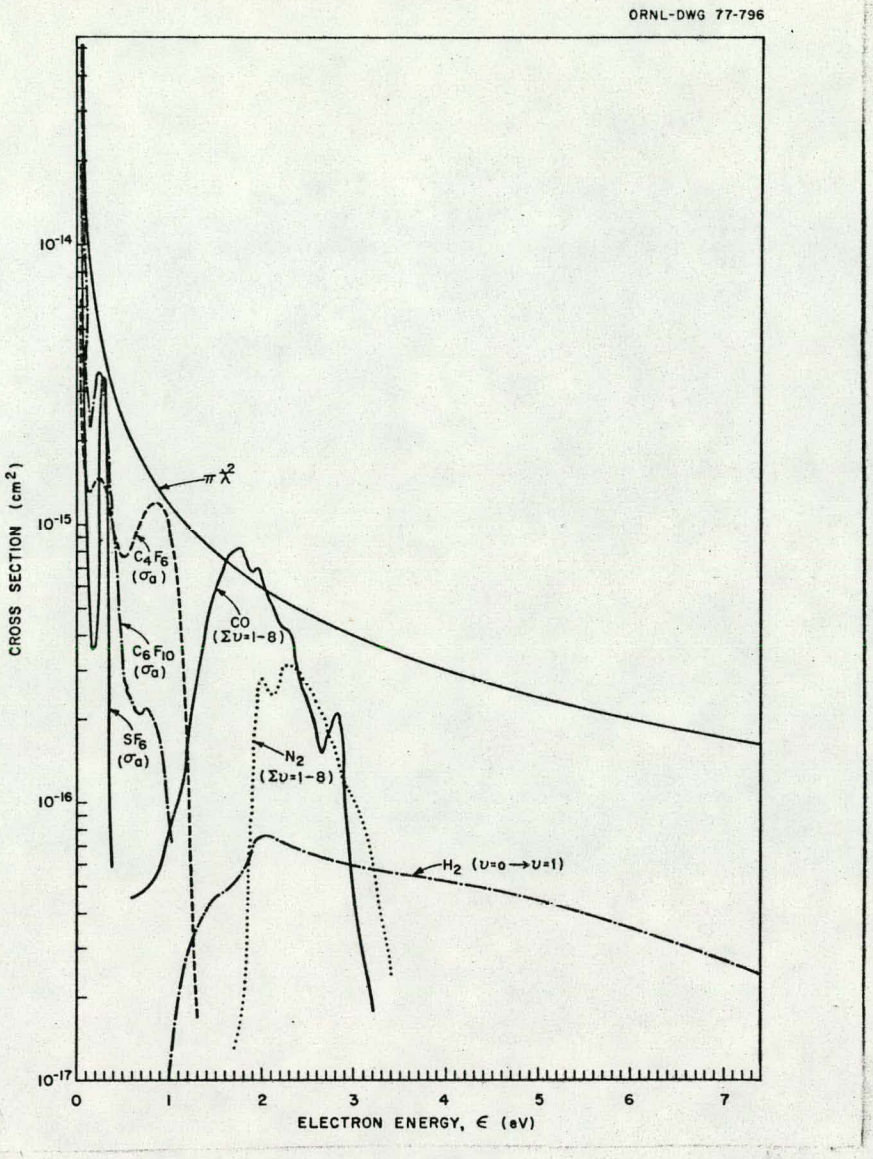

Fig. 6. Electron attachment cross sections, σ_a, as a function of electron energy, ε, for the three electron attaching gases, SF_6, C_4F_6, and C_6F_{10}, and vibrational excitation cross sections via negative ion resonances for CO, N_2, and H_2 (see text and Ref. 7).

Fig. 5 for SF_6/N_2 and c-C_4F_8/N_2 mixtures have been normalized to the nonuniform field value of the V_s for pure N_2. Although the normalized uniform and nonuniform field data are not dramatically different, it is interesting to see that the dependence of V_s on the amount of SF_6 in N_2 shows a stronger "saturation" effect in uniform than in nonuniform fields. In the uniform field case, the SF_6/N_2 mixtures which contain more than 40 to 50% of SF_6 showed little additional improvement in V_s. In the

Table 6. Effect of Negative Ion Resonances on Breakdown[a,b]

Percentage of Component Gas					Slope (kV/atm-mm)	Intercept (kV)	$(V_s)_R$[c]
C_4F_6	SF_6	H_2	N_2	CO			
10		90			4.39	0.82	0.55
10			90		6.18	0.66	0.73
10				90	6.71	1.02	0.82
33		67			8.76	0.68	1.01
33			67		8.93	1.41	1.10
33				67	10.74	0.61	1.22
66		34			15.05	0.55	1.66
66			34		14.16	0.22	1.52
66				34	16.12	0.49	1.76
	10	90			3.27	0.69	0.40
	10		90		4.83	1.18	0.60
	10			90	5.75	1.13	0.71
	33	67			4.79	1.13	0.59
	33		67		6.55	0.83	0.78
	33			67	7.18	1.04	0.86
	66	34			6.70	0.83	0.80
	66		34		7.56	1.03	0.91
	66			34	8.28	0.66	0.96
100					17.55	2.00	2.09
	100				8.49	0.87	1.00
		100			1.55	1.30	0.25
			100		2.74	1.56	0.40
				100	3.52	1.80	0.50

[a] From Ref. 4.

[b] Total pressure 2 atm; sphere-plane electrode geometry.

[c] Breakdown strength relative to SF_6 of 1.

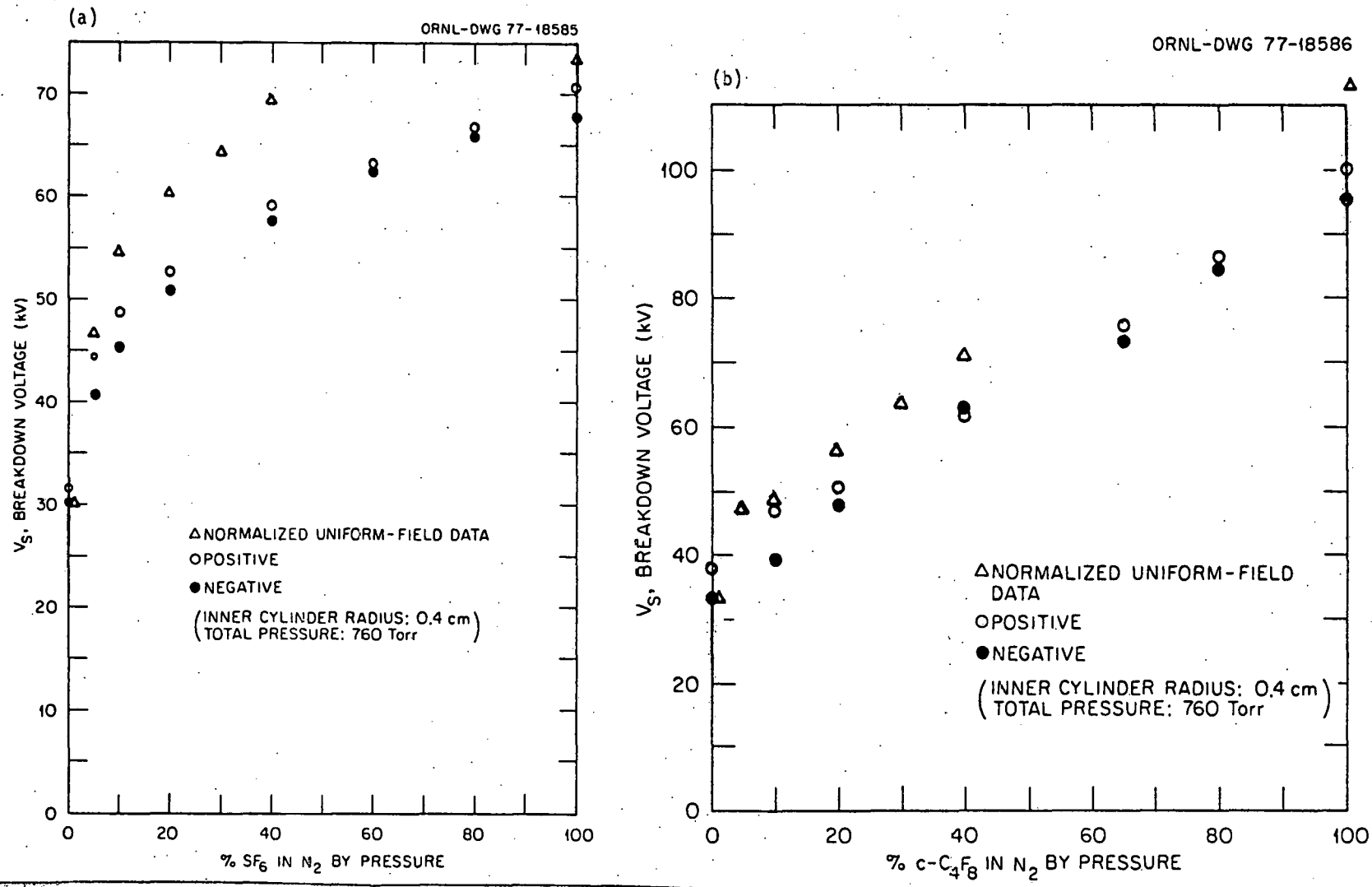

Fig. 7. a. Breakdown voltages for SF_6/N_2 mixtures with cylindrical electrode radii 0.4 and 2 cm. (o) inner electrode at positive potential, (●) inner electrode at negative potential, (Δ) normalized uniform field data. b. Breakdown voltages for c-C_4F_8/N_2 mixtures with cylindrical electrode radii 0.4 and 2 cm. (o) inner electrode at positive potential, (●) inner electrode at negative potential, (Δ) normalized uniform field data.

nonuniform fields of concentric cylinder geometries, the V_s vs % SF_6 curves exhibit less of this saturation. From similar data[4] using inner electrode radii of 1.4, 0.75, and 0.4 cm, each inside the outer cylinder of inner radius of 2 cm, it seems that the difference between the uniform and nonuniform field values of V_s increases with increasing field inhomogeneity. This could be attributed to the fact that the electron energy distribution function is shifted to higher energies in the case of nonuniform fields and to remove the same number of electrons more SF_6 is needed because the electron attachment cross section for SF_6 is small for electrons with energies $\gtrsim$0.4 eV (see Fig. 3). Consistent with this interpretation are the data in Fig. 7b on c-C_4F_8/N_2 where it is seen that when the uniform field data on V_s vs % c-C_4F_8 in N_2 are normalized to the nonuniform field data on the same system, minor differences are observed and practically no saturation effect is evident in either. The superior behavior of c-C_4F_8 compared with SF_6 is attributed to the fact that the electron attachment cross section for this molecule extends to higher energies than that for SF_6 (Fig. 3). This explanation is, however, tentative and requires further scrutiny. Our experiments so far indicate that in the nonuniform fields of concentric cylinders, c-C_4F_8, C_4F_8, and C_4F_6 continue to be far superior insulating gases to SF_6. Further work in this area and on the effect of surface roughness and electrode material on V_s is in progress at our laboratory.

ENVIRONMENTAL ASPECTS OF DIELECTRIC GASES; ANALYSIS OF BREAKDOWN PRODUCTS OF NEW GAS INSULATORS

An important consideration in the study of gaseous dielectrics is that of decomposition of the original gas/gas mixture. Decomposition results in possible loss of dielectric strength and in the possible formation of products which may be harmful to the system, to the environment or to both. Knowledge of the extent and nature of the decomposition products is necessary for any possible chemical intervention to neutralize the toxic or otherwise harmful products formed.

Presently at our laboratory a program is underway to systematically study the processes which lead from the initial electron impact induced fragmentation to the final long-lived products formed after breakdown.

There are essentially three aspects to this program: (1) determination of the initial products (parent ions, fragment ions, and radicals) resulting from single electron-molecule collisions as a function of electron energy by application of time-of-flight mass spectrometry; (2) analysis of decomposition products by a combination of gas chromatography and mass spectrometry; and (3) a study of the intermediate ion-molecule reactions which lead from the initial to the final products by high pressure mass spectrometry.

As an example to this approach, we have studied[12] C_4F_6 (perfluoro-2-butyne). The time-of-flight mass spectrum of C_4F_6 shows that low-energy ($\lesssim$10 eV) electron impact results predominantly in the formation of $C_4F_6^-$ ions, contributing >98% of all negative ions produced in this energy range. The remaining (<2%) ions consist of $C_3F_3^-$, F^-, and CF_3^- (see Table 7 and Fig. 8 for the relative intensity and energy dependence of these ions). It is thus indicated by these findings that C_4F_6 is not easily decomposed under electron bombardment. The resistance to fragmentation, seen in the C_4F_6 molecule, can be more fully appreciated when it is compared with the electron impact induced fragmentation of another good dielectric, namely, C_4F_8 (perfluorobutene-2). Perfluorobutene-2 (C_4F_8) exhibits far more extensive fragmentation (see Table 7) including the formation of $C_4F_7^-$, $C_4F_6^-$, $C_3F_5^-$, $C_3F_3^-$, $C_2F_3^-$, CF_3^-, and F^- ions with F^- being the most abundant ion in the vicinity of 5 eV. Quite unlike the results for C_4F_6, the negative ion fragments $C_4F_7^-$ and $C_4F_6^-$ were produced at near-zero energies in the case of C_4F_8. From the standpoint of initial electron impact induced fragmentation, C_4F_6 appears to be quite stable.

The problem of tracing the reaction pathways leading from the initial ion fragments to the final stable products is very complex, requiring a study of the ion-molecule reaction processes using high pressure mass spectrometry. This phase of our work in which the intermediates will be identified will be undertaken in the near future.

The last step of the decomposition problem lies in the identification and quantification of the products formed in gases which have been subjected to electrical breakdown. To accomplish this, gases which have

Table 7. Parent and Fragment Negative Ions Produced in C_4F_6 (Perfluoro-2-butyne) and C_4F_8 (Perfluorobutene-2) by Electron Impact

Negative Ion	Position of Maximum Ion Intensity	Relative Peak Ion Intensity
	C_4F_6 (perfluoro-2-butyne)	
$C_4F_6^{-*}$[a]	∿0.0	1000
$C_3F_3^-$	1.5	2.4
	5.0	4.0
CF_3^-	5.9	0.2
F^-	5.3	3.1
	C_4F_8 (perfluorobutene-2)	
$C_4F_8^{-*}$[a]	∿0.0	1000
	4.1	∿0.5
	7.4	∿0.3
$C_4F_7^{-*}$[a]	∿0.0	9.5
$C_4F_6^{-*}$[a]	∿0.0 (shoulder)	
	∿0.7	1.5
$C_3F_5^{-*}$[a]	2.3	0.8
	4.2	2.3
$C_3F_3^-$	5.1	0.9
$C_2F_3^-$	5.4	0.4
CF_3^-	5.3	1.3
F^-	5.2	26.7

[a]These ions were found to be metastable with autodetachment lifetimes $>10^{-5}$ sec.

been sparked under controlled conditions have been analyzed in a gas chromatograph followed by an ionization mass spectroscopy detection system. Preliminary work on a pure sample of C_4F_6 shows that the nontoxic[13] gases CF_4 (perfluoromethane), C_2F_4 (perfluoroethylene), and

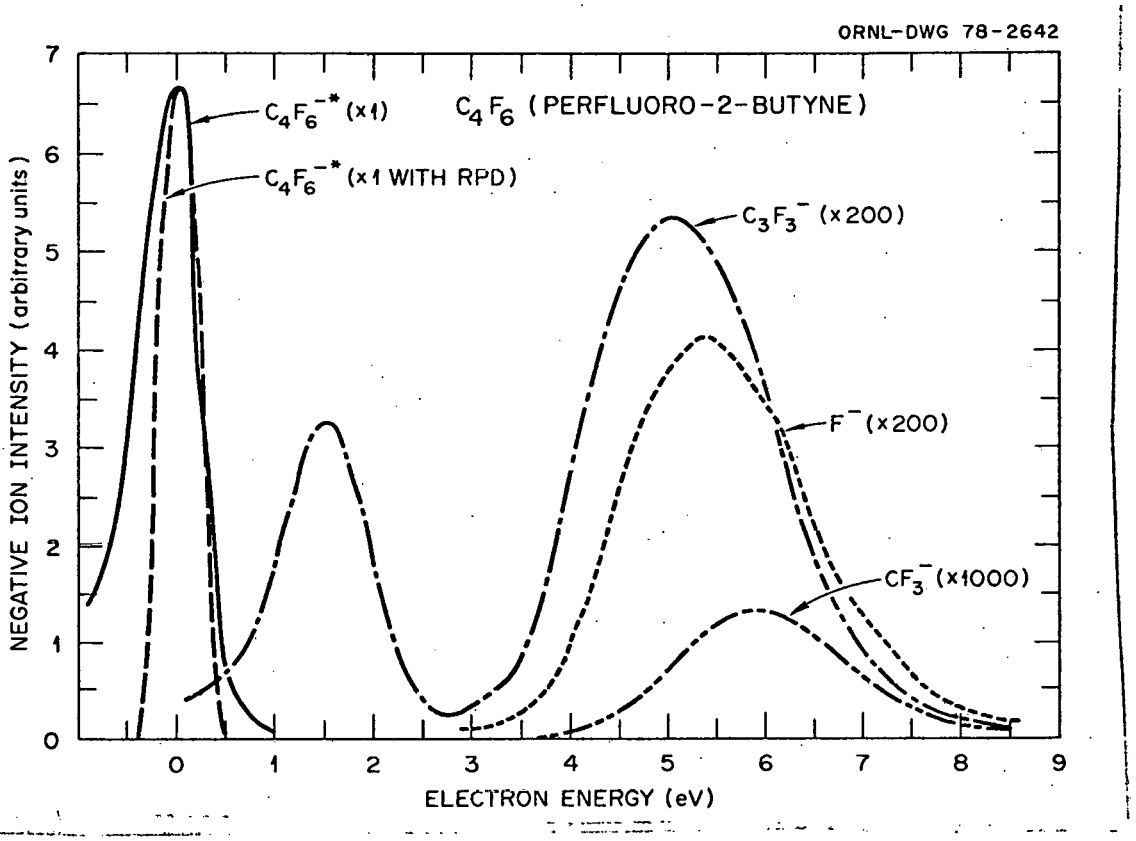

Fig. 8. Negative ion intensity as a function of electron energy for C_4F_6 (perfluoro-2-butyne). Except where noted the spectra were taken without the retarding potential difference (RPD) method.

C_2F_6 (perfluoroethane) are produced. The extent of decomposition of the dielectric as a function of the energy delivered to the system for both unitary and multicomponent gas mixtures is under investigation.

TOXICITY AND CARBON DEPOSITS

A comment on the toxicity and carbon deposits of sparked gases is in order. The toxicity of fluorocarbon compounds varies enormously with relatively small changes in their structure. Thus c-C_4F_8 is nontoxic (an 80% mixture with 20% oxygen substituted for air and breathed for four hours did not affect rats[14]), while iso-C_4F_8 (perfluoroisobutene) at 0.5 parts per million in air was found to be lethal to animals if breathed for four hours.[15]

Each new compound recommended for large-scale commercial use must be individually subjected to prior testing for toxicity. In such toxicity tests care must be taken to ensure that various compounds used as precursors in the manufacturing of fluorocarbons are eliminated, since such compounds often tend to be very toxic and trace amounts—which could be eliminated with careful manufacturing procedures—may be overlooked in small-scale laboratory preparations and can thus lead to erroneous conclusions as to the toxicity of a compound. For example, C_4F_6 samples can be contaminated with $C_4F_6Cl_2$—a known toxic compound used in the preparation of C_4F_6—which can be eliminated by a careful manufacturing procedure.

Another major problem connected with the use of perfluorocarbon compounds in electrical apparatus is the formation and deposition of carbon from the gas under an arc. This carbon can settle on insulators and short them out. Two possible ways to overcome this problem are: (1) appropriate designs of insulators which can relieve the effect of the carbon deposits on the insulators and (2) the use of SF_6 and N_2 (and perhaps other gases) in mixtures with perfluorocarbons. Such mixtures (e.g., $C_4F_6/SF_6/N_2$) can greatly reduce carbon deposits while increasing the dielectric strength above that of SF_6 (see Ref. 4).

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