

REVIEW

RECENT ADVANCES IN GASEOUS DIELECTRICS
AT OAK RIDGE NATIONAL LABORATORY*

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ABSTRACT

Recent developments in gaseous dielectrics are discussed with emphasis on dielectric gas mixtures containing SF₆. Recent findings on the isotopic, pressure, and nonuniform field dependence of the dielectric strength of gases are also presented, and ways to enhance the corona-stabilization characteristics of gas mixtures by appropriate additives (e.g. to SF₆) are outlined. In addition, results are presented on the spark decomposition products of SF₆ and the alleviation of the harmful effects of conducting particles by particle coating in situ. Finally, electron attachment, electron drift velocity, and breakdown properties of gas mixtures (e.g. C₂F₆ or C₃F₈ in Ar or CH₄) - comprised of electron attaching and electron conductivity enhancing components - which have promise for use in pulsed power technologies are reported.

GASEOUS DIELECTRICS RESEARCH

Worldwide recent efforts have unraveled many of the fundamental phenomena and basic processes which determine the dielectric properties of a gaseous medium. Fundamental research has provided sufficient knowledge on the basis of which it is now possible to choose and to tailor gaseous dielectrics for the varied needs of the electric power industry (e.g., power transmission and distribution, circuit breakers, transformers, high voltage research equipment, pulsed power technologies) which require freedom in the choice of gas. A number of these advances can be found in the proceedings of the many international meetings on the subject, especially the International Symposia on Gaseous Dielectrics [1,2], the International Conferences on Gas Discharges and Their Applications [3], the International Symposia on High Voltage Engineering [4], and the International Conferences on Phenomena in Ionized Gases [5].

Selected recent advances taken mostly from the authors' work at Oak Ridge National Laboratory (ORNL) are discussed in this paper.

TAILORING OF GASEOUS DIELECTRICS FROM KNOWLEDGE OF THEIR BASIC PROPERTIES

Knowledge of the electron-attaching, electron-slowing-down, and electron-impact-ionization properties of gases allows one to choose and to tailor gaseous dielectrics. This can be seen by referring to Fig. 1. In a gas - at a number density N - under an applied electric field E , the free electrons attain an equilibrium energy distribution $f(\epsilon, E/N)$ which is a function of the gas and E/N . When the value of E/N is low (e.g., 1.24×10^{-16} Vcm² in Fig. 1 for N₂), $f(\epsilon, E/N)$ lies at low energies, and the number of electrons capable of ionizing the gas is negligible (i.e., the gas is an insulator). As the voltage is increased, however, $f(\epsilon, E/N)$ shifts to higher energies ϵ and for sufficiently high E/N the number of electrons capable of ionizing the gas is such that the gas makes the transition from an insulator to a conductor (i.e., it breaks down). In Fig. 1 $f(\epsilon, E/N)$ is shown for N₂ at the limiting value of E/N , $(E/N)_{lim} (\approx 1.3 \times 10^{-15}$ Vcm²) (i.e., the value of E/N at which breakdown occurs). Even at this high E/N value only a small fraction of electrons possesses sufficient energy to induce ionization. This is designated in Fig. 1 by the shaded area α which is a measure of the ionization coefficient, α/N , expressed as

$$\alpha/N = (2/m)^{0.5} w^{-1} \int_{I_0}^{\infty} \underbrace{f(\epsilon, E/N) \epsilon^{0.5} \sigma_i(\epsilon)}_I d\epsilon \quad (1)$$

where I_0 is the ionization threshold energy, m is the electron mass, w is the electron drift velocity, and $\sigma_i(\epsilon)$ is the electron-impact-ionization cross section.

The most effective way to prevent electrons from initiating breakdown is to remove them by attachment to the gas molecules forming stable negative ions. In Fig. 1 is shown the total attachment cross section, $\sigma_a(\epsilon)$, for SF_6 . In general $\sigma_a(\epsilon)$ is large at very low energies, and thus only electrons with energies at the extreme low-energy range can be removed efficiently by electron attachment. The shaded area in Fig. 1 designated by η is a measure of the effective electron attachment coefficient, η/N_a , expressed as

$$\eta/N_a = (2/m)^{0.5} w^{-1} \int_0^{\infty} \underbrace{f(\epsilon, E/N) \epsilon^{0.5} \sigma_a(\epsilon)}_A d\epsilon \quad (2)$$

where N_a is the attaching gas number density ($N=N_a$ for a unitary electronegative gas). Knowledge of α/N and η/N_a allows one to predict $(E/N)_{lim}$, which for uniform fields is defined as the value of E/N at which $\alpha=\eta$.

The gas dielectric strength can be optimized by maximizing the quantity A and by minimizing the quantity I . For this, not only must $\sigma_a(\epsilon)$ be as large as possible and $\sigma_i(\epsilon)$ as small as possible, but also the reduction of the electron energies is of paramount significance because a lower-lying $f(\epsilon, E/N)$ minimizes I and maximizes A .

The significance of $\sigma_a(\epsilon)$ has been well documented [7]. To achieve a high dielectric strength, one must employ an "electronegative" gas (i.e., a gas which forms stable negative ions). This can be seen from Fig. 2. As the attachment rate constant $k_a(\langle\epsilon\rangle)$ increases, so does the breakdown voltage V_B relative to SF_6 . Knowledge of $\sigma_a(\epsilon)$ led to the identification of many excellent unitary gas dielectrics such as the perfluorocarbons listed in Table 1.

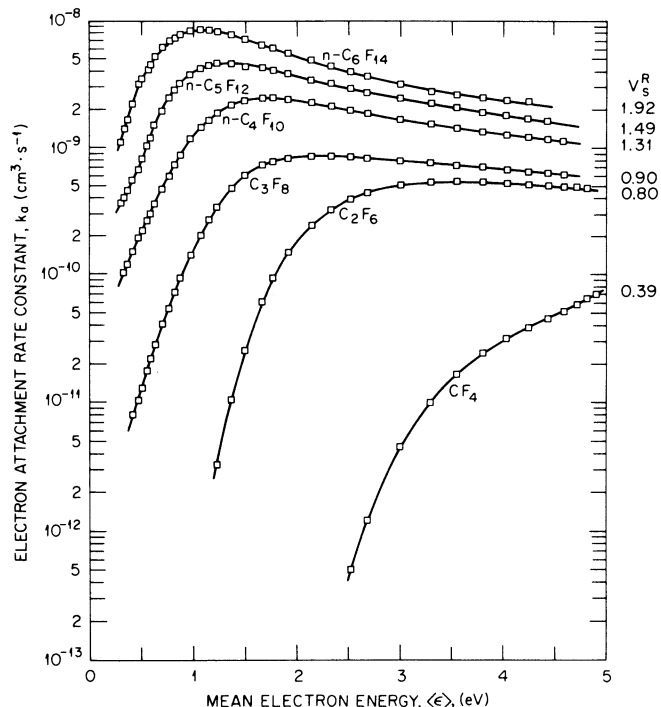


Fig. 2: k_a versus $\langle\epsilon\rangle$ for the perfluoroalkanes C_NF_{2N+2} ($N = 1$ to 6) (Refs. 8,9) and their dc uniform electric strengths [9,10] relative to SF_6 .

Table 1
DC Relative Dielectric Strengths, V_R ,
of Perfluorocarbons [7,10]

	V_R
SF_6	1.0
c- C_4F_8 (perfluorocyclobutane)	1.2-1.3
2- C_4F_8 (perfluoro-2-butene)	1.7
1,3- C_4F_6 (perfluoro-1,3-butadiene)	1.5
c- C_4F_6 (perfluorocyclobutene)	1.7
2- C_4F_6 (perfluoro-2-butyne)	2.2-2.4
c- C_5F_8 (perfluorocyclopentene)	2.1-2.2

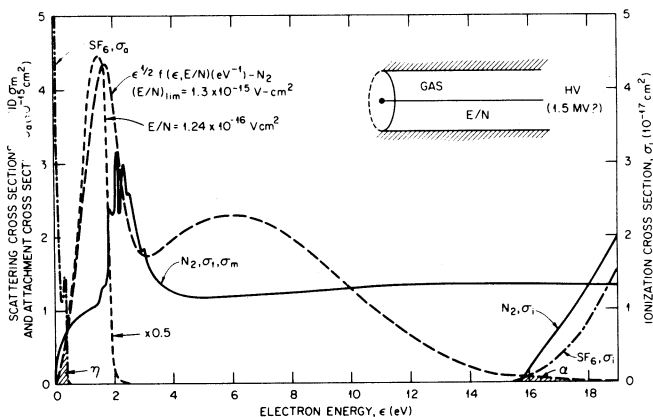


Fig. 1: Ionization cross section $\sigma_i(\epsilon)$ for N_2 and SF_6 close to the ionization onset. Electron scattering cross section as a function of ϵ for N_2 and electron attachment cross section σ_a for SF_6 . Normalized electron energy distribution function $\epsilon^{0.5}f(\epsilon, E/N)$ as a function of ϵ for N_2 at two values of E/N (see text; from Ref. 6).

The basic principles embodied in Fig. 1 can be used to tailor binary gas mixtures with, often, substantial synergistic effects [synergism is defined here as the difference in the measured breakdown voltage, $(V_B)_{mix}$, of the mixture and the partial-pressure-weighted breakdown voltages of the component gases]. The observed synergistic effects for binary gas mixtures containing electronegative and nonelectronegative (buffer) components generally fall into three categories:

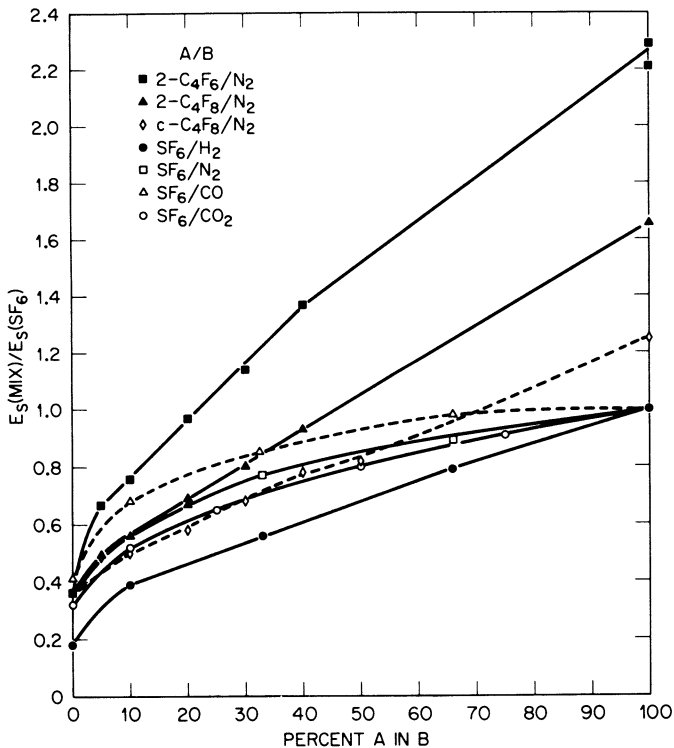


Fig. 3: $E_s(MIX)/E_s(SF_6)$ for electronegative/buffer gas binary mixtures [■, ▲, ◆ (dc; plane-plane geometry; 66.7 kPa) [11]; ●, □, △, ○ (ac; sphere-plane geometry; 150, 203 kPa) [15a]].

Electronegative/Buffer

Here the buffer gas scatters the electrons into an energy region in which the electronegative gas attaches them efficiently. Fig. 3 shows this for the electronegative gases $c-C_4F_8$, $2-C_4F_8$, and $2-C_4F_6$ in N_2 and for SF_6 in the buffer gases H_2 , N_2 , CO , and CO_2 which slow down electrons efficiently via their strong low-lying negative ion states [11]. Fig. 4 shows similar results for the electronegative gases SF_6 and $c-C_4F_8$ in the buffer gases CHF_3 and $1,1,1-CH_3CF_3$ which slow down electrons efficiently via dipole scattering [11,12]. The $(V_s)_{mix}$ exceeds the partial-pressure-weighted V_s but not that of the electronegative component. Most of the improvement in $(V_s)_{mix}$ is exhibited for small percentages of the electronegative gas; for SF_6 in N_2 or CO , the $(V_s)_{mix}$ tends to saturate as the percentage of the electronegative component is increased.

Electronegative/Electronegative whose electron attachment rate constants $k_a(<\epsilon>)$ are independent of N

Here the $(V_s)_{mix}$ is practically equal [11] to the partial-pressure-weighted V_s (Fig. 5). This, however, is generally expected when both electronegative components are polyatomic and hence $f(\epsilon, E/N)$ is not seriously affected by their relative proportion.

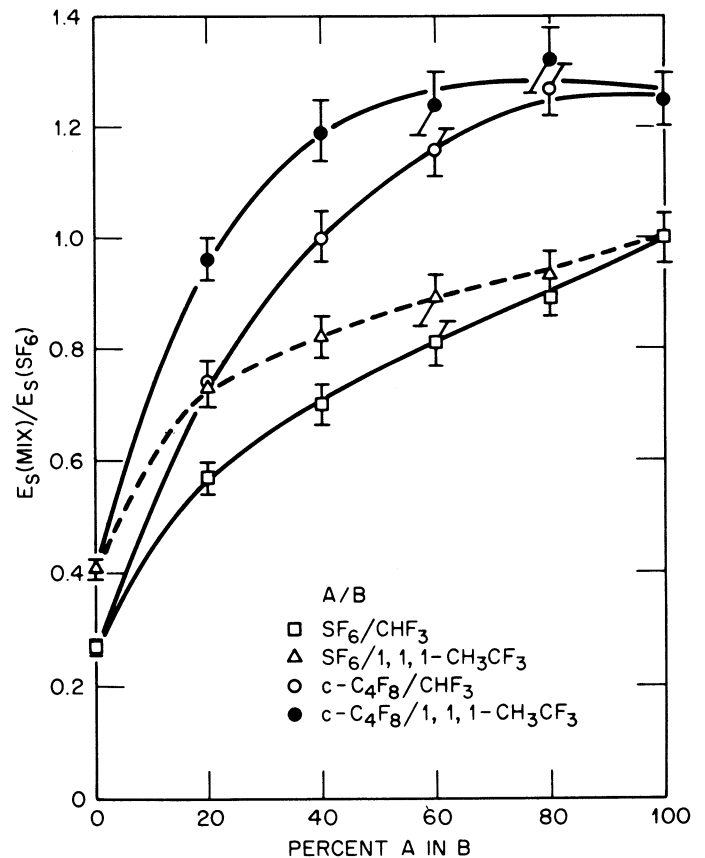


Fig. 4: $E_s(MIX)/E_s(SF_6)$ for binary mixtures of the electronegative gases SF_6 and $c-C_4F_8$ in the polar buffer gases CHF_3 and $1,1,1-CH_3CF_3$ (dc; plane-plane geometry; 66.7 kPa).

Electronegative/Electronegative for which the $k_a(<\epsilon>)$ or either or both components is a function of N

In such mixtures the $k_a(<\epsilon>)$ depends on pressure by virtue of processes which increase $k_a(<\epsilon>)$ (e.g. increased transient anion stabilization, decrease of collisional detachment by charge transfer) or decrease $k_a(<\epsilon>)$ (e.g., increased anion destruction) with increasing N . In the former case [increase in $k_a(<\epsilon>)$ with N], the $(V_s)_{mix}$ can exceed that of either component at the same pressure (Fig. 6) and in the latter case [decrease in $k_a(<\epsilon>)$ with N], a negative synergism may actually occur [13]. It should be noted that these types of synergism may also be exhibited for electronegative/buffer gas combinations when the former's electron attaching properties are strongly dependent on N .

The data in Figs. 3-6 and many other studies on these and other systems [1-4,11-15a] provided a large body of knowledge on binary gas mixtures some of which are appropriate for applications. The ORNL work [14] suggested, for example, a number of perfluorocarbon/ SF_6 , perfluorocarbon/ N_2 (or CHF_3), and SF_6/N_2 mixtures as good candidates for industrial testing and adoption. A 50% $SF_6/50\% N_2$ mixture at 15% higher total pressure than pure SF_6 exhibits the same dielectric strength as pure SF_6 at ~35% lower cost [15]. This mixture has many other advantages (e.g., with respect to dewpoint, nonuniform field behavior, and particle effects) that make it the strongest candidate yet to replace pure SF_6 in practical equipment. For this reason SF_6/N_2 mixtures must

be studied more systematically in the pressure range 0.1 to 1 MPa (see Particle Control Methods).

Ternary gaseous dielectrics have been developed also in order to optimize as many of the desirable properties and characteristics of the total system as possible and at a minimum cost. For example, Christophorou et al. [14] proposed ternary gaseous dielectrics composed of N_2 , SF_6 , and small amounts of electronegative perfluorocarbons. The reasons for choosing these components and composition guidelines for such systems are given in Table 2. Of particular interest are the $N_2/SF_6/c-C_4F_8$ mixtures.

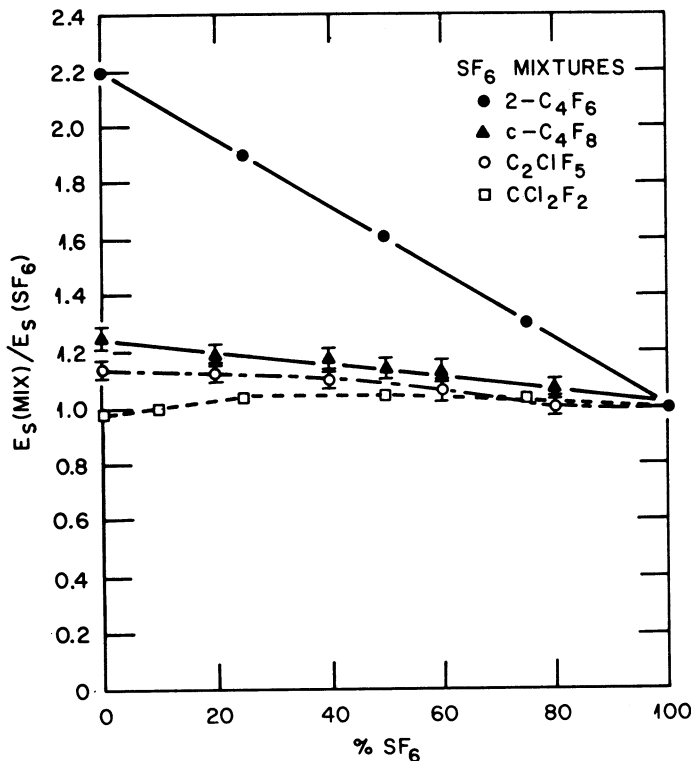


Fig. 5: $E_s(MIX)/E_s(SF_6)$ for binary mixtures of electronegative gases whose $k_{\alpha}(\langle \epsilon \rangle)$ is independent of N [●, □ (ac; sphere-plane geometry; 150 kPa) [15a]; ▲, ○ (dc; plane-plane geometry; 66.7 kPa) [11]].

ISOTOPIC DEPENDENCE OF THE BREAKDOWN STRENGTH OF GASES

An isotopic dependence of the dc breakdown voltage V_s has recently been discovered for both quasi-uniform and highly nonuniform fields (see caption of Fig. 7) using the pairs of molecules H_2/D_2 , CH_4/CD_4 [16] and NH_3/ND_3 [17]. The results on H_2/D_2 and CH_4/CD_4 are shown in Fig. 7. For quasi-uniform fields the V_s of the lighter molecules for each of the three pairs is slightly higher than for the corresponding heavier species. However, for the highly nonuniform fields of point-plane geometry, while the V_s of H_2 (and NH_3) still exceeds that of D_2 (and ND_3), the V_s of CH_4 is substantially lower than that of CD_4 . The former ($V_{s,H} > V_{s,D}$) isotope effect has been called *direct* and has been attributed [16] to the higher ionization coefficients for the deuterated species

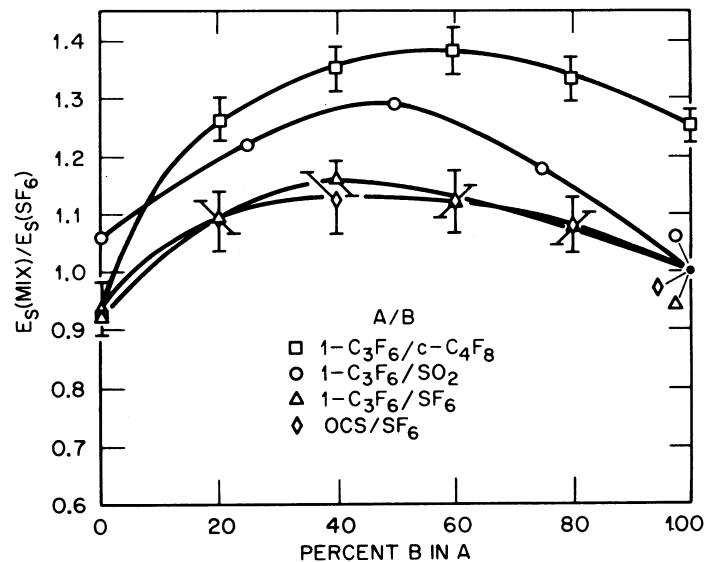


Fig. 6: $E_s(MIX)/E_s(SF_6)$ for binary mixtures of electronegative gases for which the $k_{\alpha}(\langle \epsilon \rangle)$ of either ($1-C_3F_6$) or both ($1-C_3F_6$; SO_2) components is a function of N (Ref. 11) [■, ▲ (DC; plane-plane geometry; 66.7 kPa) [11]; ○ (AC; sphere-plane geometry; 150 kPa) [15a]; ◇ (DC; sphere-sphere geometry; 66.7 kPa) [11]].

compared with the nondeuterated. The latter ($V_{s,H} < V_{s,D}$) has been called *inverse* isotope effect and cannot be explained on such a basis. It has been suggested [16] that the inverse isotope effect may result from differences in the electron-impact-induced dissociation processes of the isotopic pairs of molecules - the cross sections for electron-impact-induced dissociation are much larger for CH_4/CD_4 [18] than for H_2/D_2 [19]. The inverse isotope effect is substantial and may find application in isotope separation.

EFFECT OF PRESSURE ON THE BREAKDOWN STRENGTH OF GASES

The V_s of a number of gaseous dielectrics has recently been found to depend on the gas pressure P . A prototype of this behavior is the gas $1-C_3F_6$ (perfluoropropylene). The $(E/N)_{lim}$ versus P for $1-C_3F_6$ and SF_6 [9] is shown in Fig. 8. It is seen that while for SF_6 the $(E/N)_{lim}$ is independent of P , for $1-C_3F_6$ it increases considerably with increasing P . The latter behavior has been attributed [9,20] to the increase with P of the attachment rate constant for this gas (Fig. 9). Other studies [21,22] confirmed the results in Fig. 8, which are also consistent with the distinct synergism observed for the $1-C_3F_6/SF_6$ mixtures (Fig. 6). The saturation in the dependence of $(E/N)_{lim}$ on P is related to the saturation of the increase of $k_{\alpha}(\langle \epsilon \rangle)$ with increasing P . The behavior of this gas and its mixtures with SF_6 in both uniform (Fig. 8) and nonuniform (Fig. 10) fields makes it a good candidate for applications at least for pressures up to ~ 0.4 MPa [9,23].

Table 2

Ternary Gas Dielectrics; Choice of Components: N_2 -- SF_6 --PFC^a• N_2

- Cheap, inert, abundant
- Good electron-moderating gas
- Ideal buffer gas to mix with attaching gases whose $\sigma_a(\epsilon)$ peak at ~ 0.0 eV (and thus are very large)
- Synergistic with SF_6 and many PFCs

• SF_6

- Widely used and accepted; has many desirable properties
- Ideal to mix with N_2
- Certain deficiencies (e.g., sensitivity to particles and nonuniform fields, corrosive, and toxic by-products) can be alleviated in mixtures

• PFC (e.g., $c-C_4F_8$; $2-C_4F_6$; $n-C_4F_{10}$; $2-C_4F_6$; $1-C_3F_8$)

- Excellent dielectric strength (often 2 to 2.5 that of SF_6)
- $\sigma_a(\epsilon)$ exceedingly large to high ϵ (thus complement SF_6)
- Act synergistically with N_2 and SF_6
- Certain of their problems (e.g., carbonization, cost, low P) can be alleviated in mixtures
- Help reduce or alleviate corrosive SF_6 by-products
- Improve impulse withstand voltage characteristics
- Could alleviate conducting particle effects by particle coating *in situ* and thus drastically increase V_s

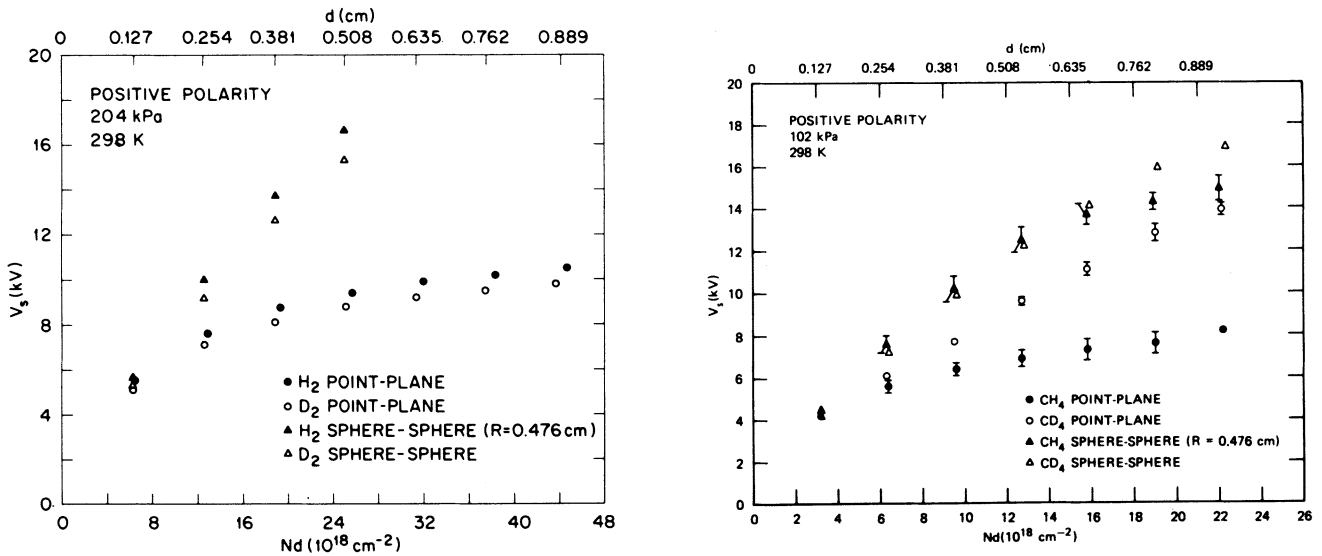
Composition Guidelines N_2 : As much as possible ($\geq 60\%$)PFC: As low as possible (~ 5 to 20%) SF_6 : Amount necessary to optimize system (~ 20 to 30%)^aElectronegative perfluorocarbon.

Fig. 7: V_s versus N_d for H_2 and D_2 (left) and CH_4 and CD_4 (right) [16]. The point electrode was an 0.5-cm-diameter rod with a 30° cone terminating into a hemispherical tip with a radius of 0.1 cm. The plane electrode had a diameter of 2.8 cm and a hemispherical edge with a radius of 0.3 cm. The sphere electrodes consisted of a pair of identical spheres of 0.476-cm radii. All electrodes were highly polished. For each set of data either new electrodes or used electrodes which were polished and cleaned were used.

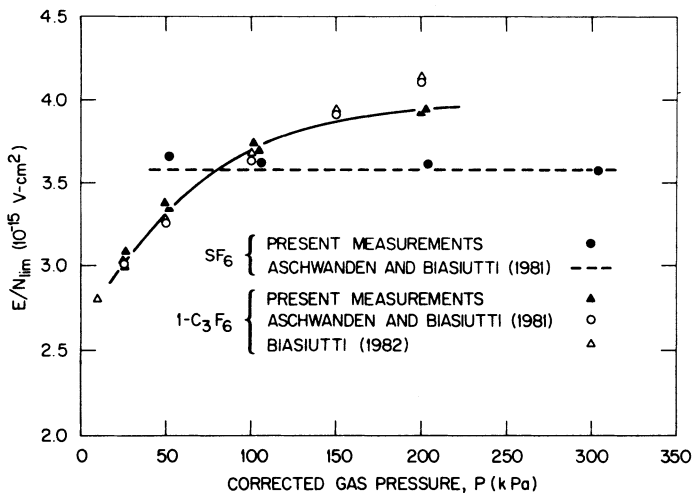


Fig. 8: $(E/N)_{lim}$ versus P (corrected for compressibility) for SF_6 and $1-C_3F_6$ (Ref. 9).

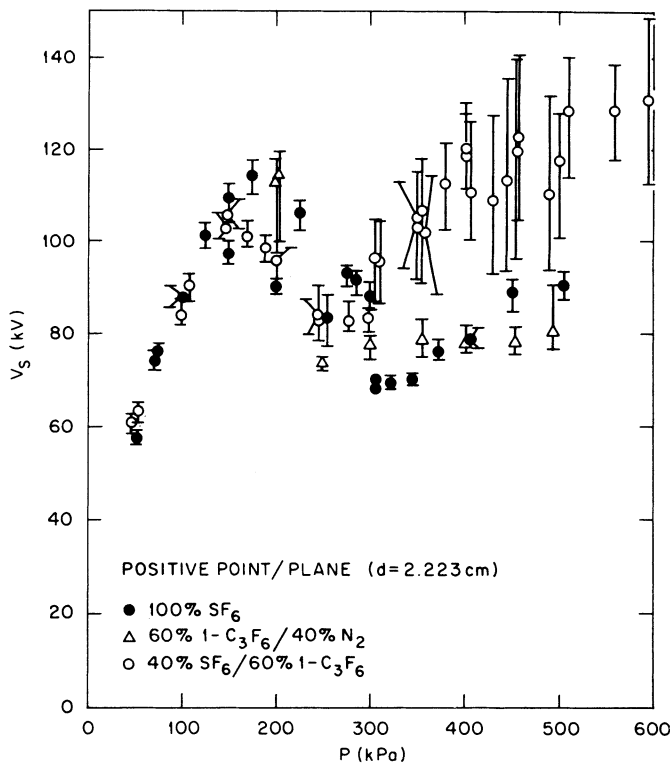


Fig. 10: V_S versus P for SF_6 and mixtures of $1-C_3F_6$ with N_2 or SF_6 under nonuniform field conditions (positive point-plane geometry) [9].

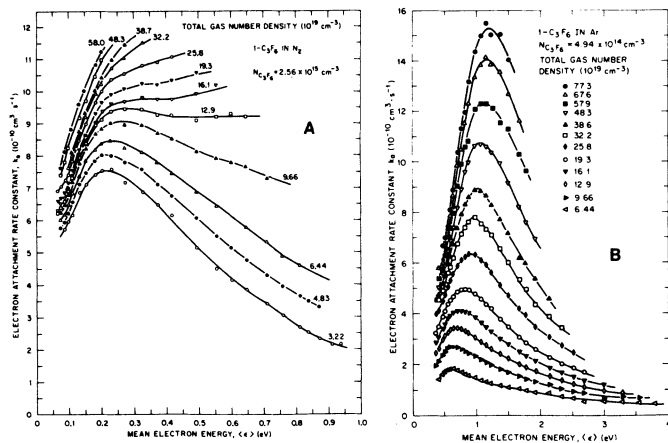


Fig. 9: $k_a(\langle \epsilon \rangle)$ for $1-C_3F_6$ in the buffer gas N_2 (A) and Ar (B) [20].

The violation of Paschen's law observed for $1-C_3F_6$ is not restricted to only this gas. Actually, it should be exhibited by other gases/mixtures whose electron attachment properties are functions of P . Thus, a similar behavior has been exhibited by C_3F_8 [21,24], $n-C_4F_{10}$ [24], N_2O [21], and SO_2 [24]; the attachment rate constants of C_3F_8 and $n-C_4F_{10}$ [8,9], N_2O [25], and SO_2 [26] also increase with N .

From the practical point of view, knowledge of the density dependence of gases can help optimize the relative proportions and total pressure of gas mixtures for maximum dielectric strength.

DIELECTRIC STRENGTH OF GASES UNDER NONUNIFORM FIELD AND IMPULSE CONDITIONS

In gas-insulated equipment, highly nonuniform fields exist (e.g., locally at surface protrusions, conducting particles, sharp edges, etc.), and the insulating

properties of the gaseous medium under such conditions are of extreme practical significance. The results - principally on SF_6 and SF_6 mixtures - of many investigators in this area are rather difficult to compare owing to the varied experimental conditions employed, especially with regard to the electrode geometry, polarity, type of voltage, and the rise time of the voltage pulse in the case of the impulse studies. Nevertheless - with the possible exception of steep-fronted pulses - these studies revealed a common feature in the V_S versus P characteristic of electronegative gases/mixtures which is exemplified schematically in Fig. 11: The V_S exceeds the corona onset voltage V_0 up to a given "critical" pressure P_c beyond which $V_S=V_0$. The pressure range over which $V_S>V_0$ is known as the corona-stabilization region. The size and shape of this region and the value of P_c are functions of the field uniformity; type, shape, and polarity of the applied voltage; and the gas composition. It is generally thought that the enhancement in corona stabilization is effected by increasing the homopolar charge near the high-stress electrode (i.e., increasing the negative space charge for negative polarity and by increasing the positive space charge for positive polarity). The former can be achieved by highly electronegative additives, especially those whose attachment cross section, $\sigma_a(\epsilon)$, extends to higher energies than that of SF_6 [14,27], while the latter may be achieved by increased ionization by additives, X , of lower ionization onset $(IO)_X$ compared with that of SF_6 [28,29].

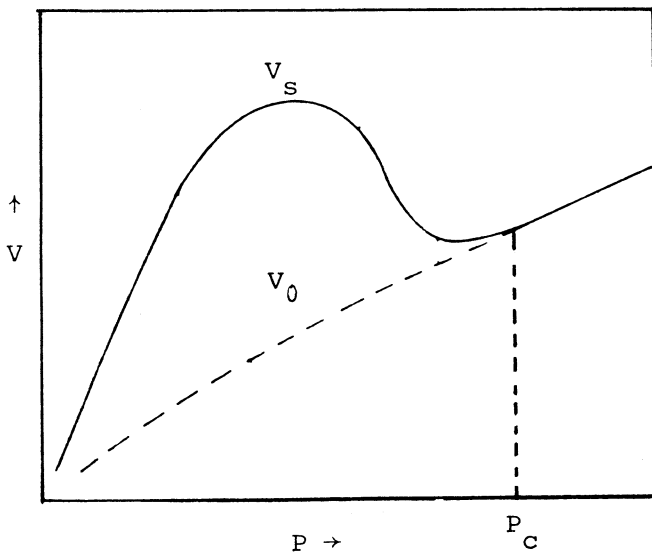


Fig. 11: Corona-Stabilized Breakdown Characteristics (see text).

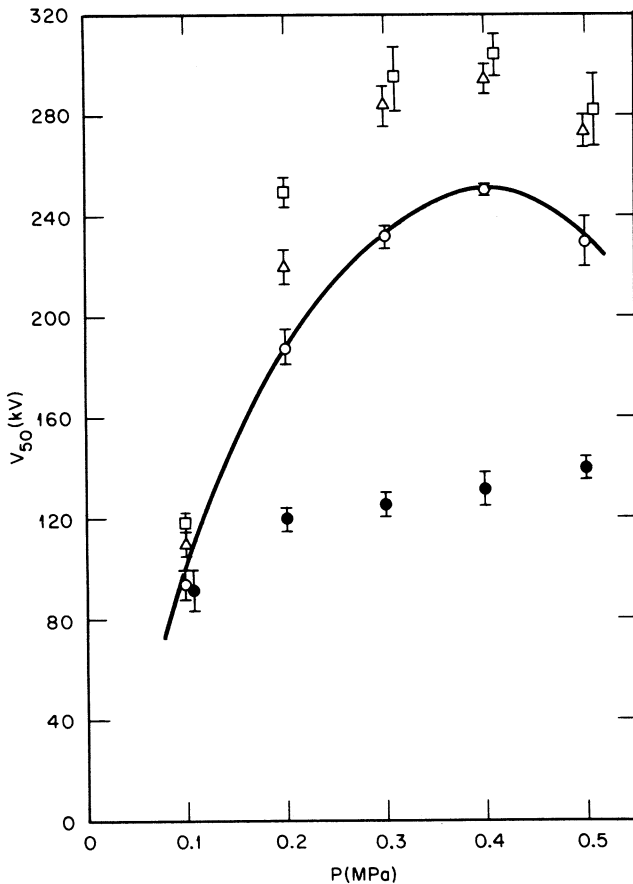


Fig. 12: V_{50} versus P for negative polarity lightning impulse; "point"-plane electrode geometry; (●) 40% $\text{SF}_6/60\% \text{N}_2$; (○) 5% $2\text{-C}_4\text{F}_8/35\% \text{SF}_6/60\% \text{N}_2$; (△) 20% $2\text{-C}_4\text{F}_8/20\% \text{SF}_6/60\% \text{N}_2$; (□) 40% $2\text{-C}_4\text{F}_8/60\% \text{N}_2$ (Ref. [14]).

In view of the significance of the corona-stabilization region in the reliability of gas-insulated equipment, recent systematic studies have been undertaken to tailor gaseous dielectrics with such a property (reliability is increased by corona stabilization because it depends on the probabilities of breakdown under various stress conditions, and corona enhancement can only decrease these probabilities). At ORNL the effort in this area has focused on increasing the corona stabilization region for SF_6 and SF_6/N_2 mixtures for both polarities: By addition of small ($\approx 20\%$) amounts of perfluorocarbons which are more efficient than SF_6 in attaching higher-energy electrons for negative polarity and by addition of low $(IO)_X$ additives in the case of positive polarity to increase, respectively, negative and positive space charge. A number of such mixtures for negative dc and impulse (switching and lightning) voltages have been developed (Fig. 12) [14,27]. Often as little as 1 to 5% of a suitable electronegative perfluorocarbon additive can effect a substantial increase in the corona stabilization. However, for such mixtures the positive polarity is usually lowered compared with SF_6 or SF_6/N_2 [14,27]. On the other hand, it has been shown [28, 29] that an increase in positive polarity corona stabilization can be effected by adding to SF_6 or SF_6/N_2 small amounts of low $(IO)_X$ additives. An example is shown in Fig. 13a for $X = \text{cis-2-C}_4\text{H}_8$ whose $(IO)_X = 9.12$ eV. This additive also causes a modest increase in the negative corona stabilization but lowers the negative corona onset compared with pure SF_6 (Fig. 13b).

If the observed corona-stabilized breakdown for positive polarity is attributed to increased positive space charge by increased ionization in the mixture, what are the possible sources of such increase in ionization? Identification and quantification of these sources is presently difficult, hindered in part by the absence of basic knowledge on the key processes involved. However, knowledge of the ionization onsets and electron-impact-ionization cross sections for SF_6 and X , and the energy positions of the electronic states and the vacuum ultraviolet absorption spectrum of SF_6 allows some tentative conclusions to be drawn [the $(IO)_{\text{SF}_6} \approx 15.7$ eV; photoabsorption [30-32] and electron energy loss [33] studies of SF_6 revealed at least four electronic states at ≈ 7 , 11.8, 13.3, 14.3, and ≈ 15 eV]. Thus, increased ionization for SF_6/X mixtures can result from (1) ionization of X by free electrons with energies between $(IO)_X$ and $(IO)_{\text{SF}_6}$ (such electrons can ionize efficiently X [34] but not SF_6) and (2) Penning ionization of X (i.e., $\text{SF}_6^* + X \rightarrow \text{SF}_6 + X^+ + e$). Both (1) and (2) can lead to a substantial increase in ionization for the mixture in view of the high $(IO)_{\text{SF}_6} \approx 15.7$ eV. Another process, namely, ionization of X by photons [i.e., $\text{SF}_6^* \rightarrow \text{SF}_6 + h\nu$ ($>(IO)_X$) followed by $h\nu + X \rightarrow X^+ + e$] seems to us unlikely since even if such energetic photons, e.g. $h\nu \approx 9.12$ eV $\approx (IO)_{\text{cis-2-C}_4\text{H}_8}$, were produced in pre-breakdown, they would most probably be reabsorbed by SF_6 itself because of its large photoabsorption cross section [30-32] and its preponderance in the mixture. A quantitative assessment of the role of these processes requires more fundamental information, for example, on the emission spectrum from SF_6 under pre-breakdown conditions and the accurate measurement of the cross section for electronic excitation of SF_6 by "threshold" electrons. It is noted that an improvement in the corona stabilization for both positive and negative polarity can be achieved by an additive which is electronegative and has a low ionization potential (see also a recent discussion on corona and insulation in [35]).

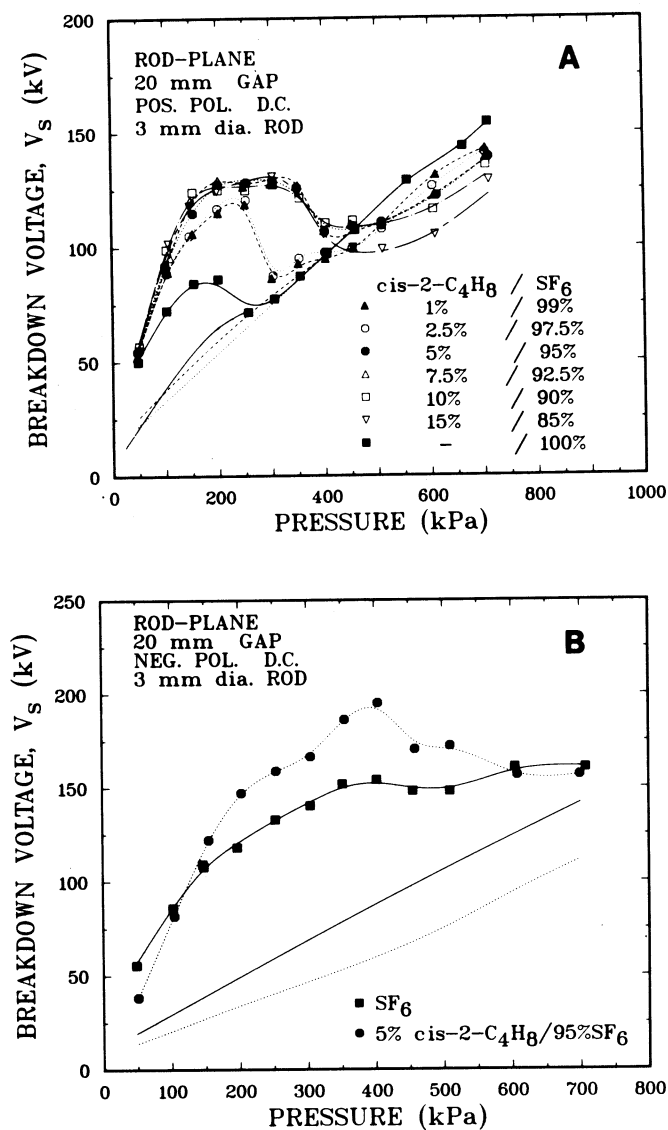


Fig. 13: Voltage-pressure characteristics in a non-uniform gap in SF₆/cis-2-C₄H₈ mixtures for positive (A) and negative (B) direct applied voltages. The lines (—) and dots (····) give the corona onsets, respectively, for SF₆ and 5% cis-2-C₄H₈/95% SF₆.

PARICLE CONTROL METHODS

As mentioned in Tailoring of Gaseous Dielectrics from Knowledge of Their Basic Properties, SF₆/N₂ mixtures have a unique potential for industrial applications; for this reason their study must be extended to higher pressures and conditions closer to those encountered in applications. In Fig. 14 are shown recent results [36] on the dc V_S of SF₆/N₂ mixtures for total pressures between 0.1 and 1 MPa. These results [37] indicate that under those conditions N₂ containing ~10% SF₆ at a total pressure twice that of pure SF₆ has the same V_S as pure SF₆, while N₂ containing 25% SF₆ at ~50% higher total pressure than pure SF₆ has the same V_S as pure SF₆.

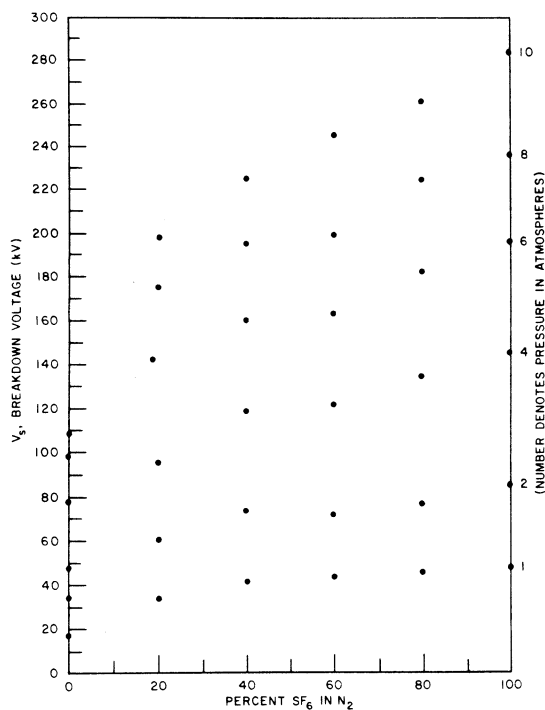


Fig. 14: V_S versus percent SF₆ in N₂ for total pressures 1, 2, 4, 6, 8, and 10 atm [36]. Concentric cylinder geometry (radii 0.75 and 2.0 cm) under dc stress; inner cylinder negative with rough surface grooves of 0.051 cm.

The effect of conducting particles on the V_S of SF₆ and SF₆/N₂ is of great practical significance. It is well known [38] that in practical uses the allowable electric stress is strongly limited by conducting particle contamination. Studies on SF₆ with ac [38-40] and dc [40] indicated that the effect of slender conducting particles (which are the most harmful) depends on the total pressure and the particle length. Recently, Pace et al. [36] used the same geometry as for the data in Fig. 14 (see figure caption) and investigated the effect of particles on the V_S of SF₆/N₂ mixtures for total pressures between 0.1 and 1 MPa. Their preliminary results are shown in Table 3. They indicate that the effect of particles depends not only on the total but also on the partial pressure; the particle effects seem to be the least at a total pressure of ~0.6 MPa and a 60% SF₆/40% N₂ gas composition for this case.

Obviously, the best way to alleviate the effect of conducting particles is to remove them from the equipment. However, in practice - and in spite of the use of "zero-field" particle-trap devices - it is impossible to remove 'all' the particles present in the system to improve its dielectric performance and reliability. For this reason we recently investigated the feasibility of two new particle-control methods [41,42]. In the first method, the particles are insulated in situ by a coating formed in a glow discharge, either before or while the 'permanent' gas insulation is in the system. The second method is to adhere the particles to an insulating material and

subsequently to contain (trap) them within the material. Each method has been found in laboratory experiments capable of completely eliminating the harmful effects of particles (see Table 4) which can otherwise reduce the dielectric strength of a gas-insulated system by factors of 2 to 10.

Insulating coating of particles in situ can be formed by using such gases as C_2F_4 , $1-C_3F_6$, $2-C_4F_8$, or $c-C_4F_8$ either by themselves at low pressure prior to introducing into the system the "permanent" insulating gas or by using them as low-concentration additives to the "permanent" gas. A number of other studies [43-45] attempted to reduce the effects of particles by coating the electrodes - rather than the

Table 3
 V_S of SF_6/N_2 Mixtures in Particle^a-Contaminated
Concentric Cylinder Geometry^b Under DC Stress

Percentage		V_S^c (kV)				
SF_6	N_2	3	4	6	8	10 atm
100	0	59.6	62.1	70.0	67.5	60.0
80	20	--	49.0	59.6	58.6	50.1
60	40	50.7	54.1	66.0	62.4	61.2
40	60	--	39.5	55.7	50.9	43.5
20	80	26.3	38.5	37.2	41.9	33.4

^aIn each test five copper particles (0.381-mm diameter \times 3.175-mm length) were placed in the gap.

^bSee caption of Fig. 14.

^cSee Fig. 14 for V_S under particle-free conditions.

Table 4
Effectiveness of Particle Coating *In Situ* and
Particle Entrapment for SF_6

System	V_S (kV)	
	1 atm	2 atm
No particles	58.1	105.9 ^a
With bare particles ^b	24.2	43.9 ^a
With coated particles ^c	60.9	106.8 ^a
Particles ^b adhered to wax ^d surface	58.6	--
Particles ^b entrapped in wax ^d	58.6	--

^aConcentric cylinder geometry (0.75- and 2.00-cm radii); negative DC.

^bFive copper particles (0.381-mm diameter \times 3.175-mm length).

^cInsulating coating formed in situ by a glow discharge in 0.1 to 0.2 kPa of $c-C_4F_8$ at ~ 0.4 mA for ~ 50 h.

^dKel-F wax (melting point 60-70°C).

particles - before installation. However, this approach was not as successful because particles could still be charged in the gas, seek weak points in the coating, and the coatings were not made in situ. It might be advantageous, nonetheless, to coat not only the particles but also all metallic surfaces (conductor and sheath) in situ because in this way the harmful effects of surface protrusions on V_S can be reduced. This would increase the maximum voltage of a gas-insulated system and thus its reliability.

In the second method investigated by Pace et al. [41,42], the particles first bounce onto the adhesive surface of an insulating material which is then temporarily melted to contain the particles within it reliably. This method requires an insulating material which is solid at the operating temperature of the system but liquid at a higher attainable temperature to facilitate particle entrapment within it. Pace et al. showed the feasibility of this method (Table 4) by using Kel-F wax. However, this material may be impractical because its melting point (60-70°C) is lower than the temperature ($\sim 100-120^\circ C$) encountered in operating equipment such as gas-insulated transmission lines. A new material developed [36] from commercial Kel-F plastic with a melting point $> 120^\circ C$ was tested at $\sim 100^\circ C$ and was found to eliminate completely the harmful effects of particles by trapping.

SPARK DECOMPOSITION OF SF_6 ; TOXICITY OF BY-PRODUCTS

Studies of the positive ions produced in SF_6 at short times ($\sim 10^{-3}$ s) following the discharge have recently been made employing a spark source and a high pressure

(up to ~100 kPa) quadrupole mass spectrometer [46-48]. These studies have shown that in sparked-purified SF₆, positive ions of the form S_xF_y⁺ (where y is either zero or odd integer, and x = 2 to 16) are observed which are practically deficient in fluorine (y/x < 2). They have also showed that the ion chemistry of SF₆ discharges is strongly dependent on gas purity. Fig. 15 shows the effect of traces of impurities on the positive ion spectrum of sparked SF₆ (P = 40 kPa). The ion S₂F₇⁺ is thought to be the precursor to many of the "terminal" ions observed in "impure" SF₆.

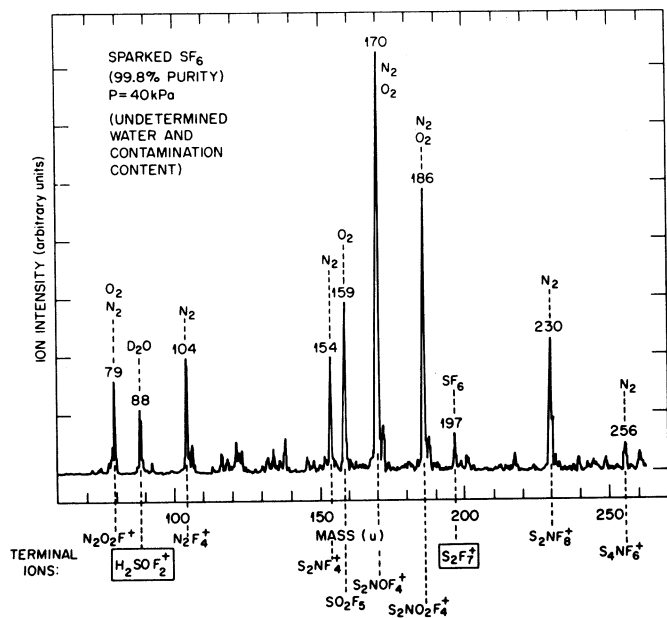


Fig. 15: Mass spectrum of positive ions produced in sparked SF₆ at 40 kPa (SF₆ purity: 99.85% by volume; undetermined water and contamination content) [46].

While the aforementioned studies are very limited, a good many studies of long-lived neutral by-products of SF₆ have been made. As can be seen from Table 5, these latter studies showed a wide variety of observed electrical-discharge-decomposition by-products of SF₆, illustrating the complexity of the decomposition mechanisms involved. Besides the work at Oak Ridge [46-49,66-68] other investigations recently have dealt with the effect of added impurities to SF₆ on the extent of its decomposition [62], on corona-induced by-product formation [65], and on the solid by-products formed in arced SF₆ [64]. As shown in Fig. 16, many of the spark-induced by-products are linked [49,66] to the initial formation of SF₄ and atomic fluorine leading to formation of SOF₂, SO₂, SiF₄, HF, and metal fluorides.

Estimates of the amounts (per unit spark energy) of some of the long-lived by-products of sparked SF₆ are listed in Table 6. The most abundant of these is SOF₂.

Most interestingly, the Oak Ridge study has shown that SF₆/perfluorocarbon mixtures permit the suppression of undesirable carbon and fluorine production through the formation of carbon fluorides [47,48,66,67]. In Fig. 17 is shown the formation of CF₄ in binary mixtures of SF₆ and 2-C₄F₈ or c-C₄F₈. Multi-component mixtures comprised of SF₆, perfluorocarbon, and a buffer gas have also been studied [66]; they can be employed to reduce overall decomposition while maintaining a high breakdown strength [14] (Table 2).

The identification of the principal long-lived spark by-products of SF₆ led us to the dual question: (1) Do these products, in the long run, affect the integrity of the dielectric and its strength? (2) Are they toxic and possibly harmful? While no answer to either question is yet complete, we investigated [68] in connection with the first question the electron-impact-induced decomposition of SF₄, SOF₂, SOF₄, and SiF₄ (see Table 7) and are in the process of measuring their dielectric strengths. In connection with the second question, we investigated the in vitro cytotoxicity of sparked SF₆ and the individual spark by-products we identified, namely, SO₂, HF, SOF₂, SO₂F₂, SiF₄, SOF₄, and SF₄ [69-71]. These latter studies have shown that although SF₆ itself is noncytotoxic, sparked SF₆ exhibits cytotoxic action which increases with increasing total spark energy (for the range 1.6-160 kJ dissipated into a cell of 60 cm³ at 133 kPa). Fig. 18 shows the increase in cytotoxicity of sparked SF₆ with increasing exposure time for a 16-kJ energy. Cytotoxicity tests on the individual sparked by-products (SO₂, HF, SOF₂, SO₂F₂, SiF₄, SOF₄, SF₄) and a 'synthetic' SF₆ mixture (comprising unsparked SF₆ plus added amounts of the identified sparked by-products in the expected concentrations) indicate the possibility that yet unidentified minor sparked by-products contribute considerably to the measured cytotoxicity of sparked SF₆ [69-71]. These observations suggest that further work is necessary to quantify the toxicity of sparked SF₆ with reference to that of better characterized gases, to establish the cause of the toxicity and to develop ameliorative procedures.

SF₆ DECOMPOSITION SCHEME

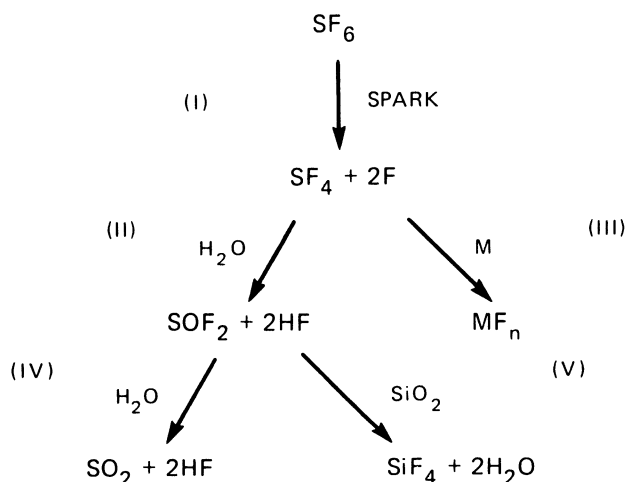


Fig. 16: Reaction scheme for sparked SF₆ leading to formation of the long-lived decomposition products SOF₂, SO₂, SiF₄, and MF_n (where M represents the electrode material; e.g., for M = aluminum the product AlF₃ is formed) [66].

Table 5
Decomposition Products Detected from Sparked SF₆ at Various Laboratories

Products	Discharge ^a	Methods ^a	Reference
SF ₂ , SF ₄ , HF, CO ₂ , H ₂ S	AC arc	IR	50
SF ₂ , SOF ₂	High current AC arc	IR	51
S ₂ F ₂	RF electrodeless	IR	51
SO ₂ F ₂	500 W AC arc	IR	52
SOF ₂ , SO ₂ F ₂	1-3 kA AC arc	MS	53
SOF ₂ , SO ₂ F ₂ , SOF ₄	Corona	GC,IR,MS	54
SOF ₂ , S ₂ F ₂ , SiF ₄	0.75 A AC arc	MS	55
SOF ₂ , SO ₂ F ₂ , SOF ₄ , SF ₄	5-10 A AC arc	GC,IR	56
SOF ₂ , SO ₂ F ₂ , SOF ₄ , SF ₄ , S ₂ F ₁₀ , S ₂ F ₁₀ O	CD	GC,IR	56
SOF ₂ , SO ₂ F ₂ , SOF ₄ , HF, WF ₆	400-500 A AC arc	GC,IR	57
SOF ₂ , SO ₂ F ₂ , CF ₄ , SiF ₄ , HF (cell not dried)	30 kA AC arc	NMR	58
SF ₄ , S ₂ F ₂ , SOF ₂ , WF ₆ , SiF ₄ , COF ₂ , CF ₄ (cell dried)	30 kA AC arc	NMR	58
SF ₄ , SOF ₂ , SOF ₄ , S ₂ F ₂ , S ₂ F ₁₀	Various	GC	59
SOF ₂ , SO ₂ F ₂ , SOF ₄ , SiF ₄ , F ₂	RF electrodeless	GC,IR,MS	60
S	RF electrodeless	EPR	61
SF ₄ , SOF ₂ , SO ₂ F ₂ , SOF ₄	0.2 A AC arc	GC,MS	62
SF ₄ , SO ₂ F ₂ , CF ₄ , CO ₂	1.8 kA AC arc	GC	63
AlF ₃	Arc	PD	64
H ₂ O, SOF ₂ , SO ₂ F ₂ , SOF ₄	DC corona	GC,MS	65
SF ₄ , SOF ₂ , SO ₂ , SO ₂ F ₂ , SOF ₄ , SiF ₄ , HF, WF ₆	Spark	MS	47,49

^aIR, infrared spectroscopy; MS, mass spectrometry; GC, gas chromatography; CD, capacitance discharge; NMR, nuclear magnetic resonance; EPR, electron paramagnetic resonance, PD, particle detector.

GASES (WITH CONDUCTOR/INSULATOR PROPERTIES) FOR PULSED POWER TECHNOLOGIES

In a number of technologies a gas is needed which is both a good conductor and a good insulator. For example, in pulsed power technologies (e.g., inductive storage) the key element is a fast repetitive switch, the successful operation of which is the availability of a gas which in the conducting (storing) stage is a good conductor and in the transferring stage (when the stored energy is transferred to the load) is a good insulator. To optimize conduction under the low E/N conditions of the conducting stage, the electrons produced by the external source (e -beam or laser) must remain free and must have as large a drift velocity w as possible. To optimize the insulating properties under the high E/N conditions of the transferring stage, the gas must effectively remove electrons by attachment (have a large attachment rate constant at high E/N). These requirements are schematically

illustrated in Fig. 19. Gases have been tailored with both characteristics [6,72,73]. The conducting stage properties were optimized by mixing a polyatomic gas (e.g., C₂F₆ or C₃F₈) which scatters effectively slow electrons into the cross section minimum of Ar (at ~ 0.3 eV) or CH₄ reducing in this way the total scattering cross section and thus maximizing w (see examples in Figs. 20 and 21). The dielectric strength was optimized by requiring that the gases which give a maximum in w and do not capture low-energy electrons (characteristic of the conducting stage), do capture very efficiently higher-energy electrons which are present in the transferring stage of the switch (Fig. 22). In this way mixtures have been developed for switching devices consisting of Ar (or CH₄) and C₂F₆ (or C₃F₈) which exhibit very large ($>1 \times 10^7$ cm s⁻¹) w at E/N values appropriate for the conducting stage of the switch and simultaneously have high dielectric strengths to sustain the (induced) high voltages encountered in practical uses in the transferring stage of the switch. It can be seen from Fig. 23 that as little as 5% of

C₂F₆ or C₃F₈ in CH₄ and about 15 to 20% of C₂F₆ or C₃F₈ in Ar yield mixtures with both required characteristics (high V_S and large conductivity) for practical devices.

Table 6

Estimates of the Amounts of the Major SF₆ Spark By-Products Formed in a Stainless Steel Electrode Cell (Energy/Spark: 0.5-14.5 J; Pressure: 40-233 kPa) [49]

By-Product	Amount (10 ⁻⁹ moles/J)
SOF ₂	0.7 -2.8
SOF ₄	0.2
SiF ₄	0.02-0.1
SO ₂ F ₂	0.014
SO ₂	0.001

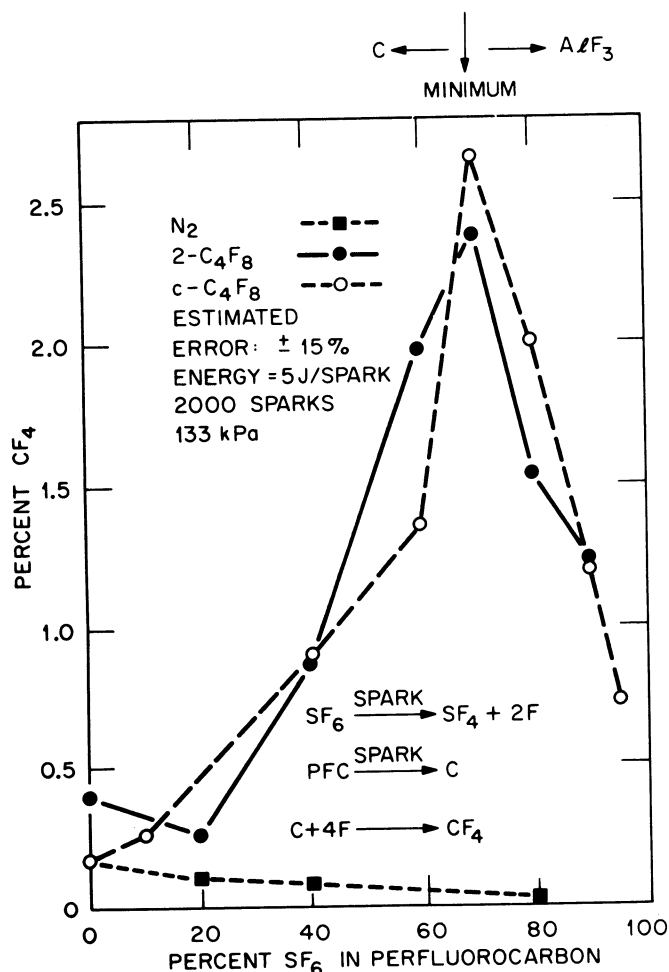


Fig. 17: Concentration (in %) of CF₄ formed in spark-induced breakdown of SF₆/X mixtures, where X = N₂ (-■-), 2-C₄F₈ (-●-), and c-C₄F₈ (-○-) [14].

TOXICITY OF SPARKED SF₆ GAS SAMPLES

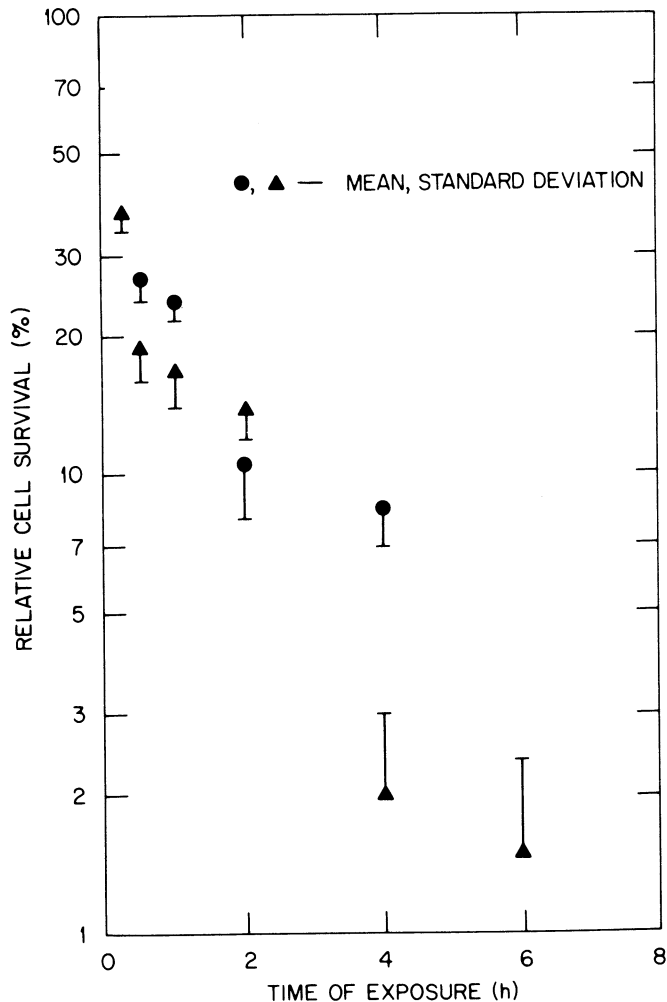


Fig. 18: Cytotoxicity of sparked SF₆ toward hamster lung cell (V79) as related to time of exposure to the gas. Relative cell survival is expressed as percentage compared with cell exposed to air. The solid symbols (●, ▲) represent two separate experiments [70].

FUTURE RESEARCH

While future research needs in this area are virtually limitless, the following areas require immediate attention:

1. Basic processes and critical data involving electrons, ions, and photons.
2. Prebreakdown and breakdown photophysics, spectral analysis of emitted light, role of photophysical processes in discharge development, photophysical diagnostics.
3. Effects of temperature and pressure on the physical, chemical, and dielectric properties of the insulating gas.
4. Studies of gaseous dielectrics with steep-fronted (μs to ns) voltage pulses.

Table 7
Results on Low-Energy Electron Impact on SF₄, SOF₂, SOF₄, and SiF₄

Negative Ion ^a (Molecule)	AO ^b (eV)	FWHM ^c (eV)	Energy at Peak (eV)	Relative Intensity	Thermochemical Results (eV)
SF ₄ ^{-*} (SF ₄)	0	Narrow ^d	~0	1000	
F ⁻ (SF ₄)	0	0.85	0.6	250	

SOF ₂ ^{-*} (SOF ₂)	0	Narrow ^d	~0	4.5	
F ⁻ (SOF ₂)	0	0.9	0.6	1000	D(SOF-F) ≤ 3.5

SOF ₃ ⁻ (SOF ₄)	0	Narrow ^d	~0	1000	EA(SOF ₃) ≈ 5.4
F ⁻ (SOF ₄)	1.9	1.25	3.2	0.14	D(SOF ₃ -F) ≤ 5.4

SiF ₃ ⁻ (SiF ₄)	10.35	0.8	11.1	1000	
F ⁻ (SiF ₄)	10.85	0.85	11.25	333	

^aThe asterisk (*) denotes that the ion is long lived with respect to autodetachment. The lifetimes of SF₄^{-*} and SOF₂^{-*} are 9.3 × 10⁻⁶ and 10 × 10⁻⁶ s, respectively.

^bAppearance onset.

^cFull width at half maximum.

^dThe profiles of these peaks were identical to that of SF₆⁻/SF₆ which is much narrower than the electron beam width [FWHM (SF₆⁻) << 0.2 eV].

5. Decomposition, reactivity, and toxicity of sparked by-products (especially of SF₆), gas recovery, heat transfer, transient gas chemistry.

6. Assessment of gas mixtures for industrial applications.

In connection with the last area (6), it seems to us that:

1. Industry should identify the specific applications that can benefit from laboratory findings and begin industrial-scale testing to verify the usefulness of proposed gas mixtures and optimize system trade-offs in design.
2. Research is needed on the reliability factors, including particle control methods, collection of data on the thermal, chemical, and environmental stability of the mixtures (and pure SF₆) under stress, and diagnostics.
3. Cooperation and interaction between the basic research and applied and industrial communities should be enhanced.

ELECTRON DRIFT/ATTACHMENT CHARACTERISTICS DESIRED IN DIFFUSE-DISCHARGE SWITCHES

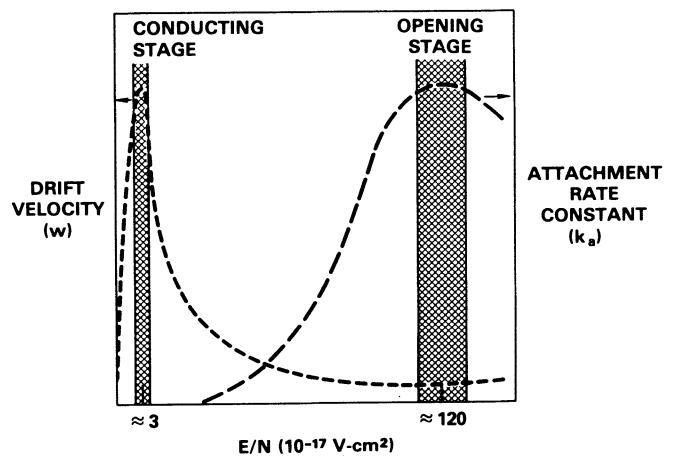


Fig. 19: Schematic illustration of the desirable characteristics of the $w(E/N)$ and $k_a(E/N)$ functions of the gaseous medium in an externally (e-beam) sustained diffuse discharge switch. Indicated in the figure are rough estimates of the E/N values for the conducting and the opening stage of the switch [6,72].

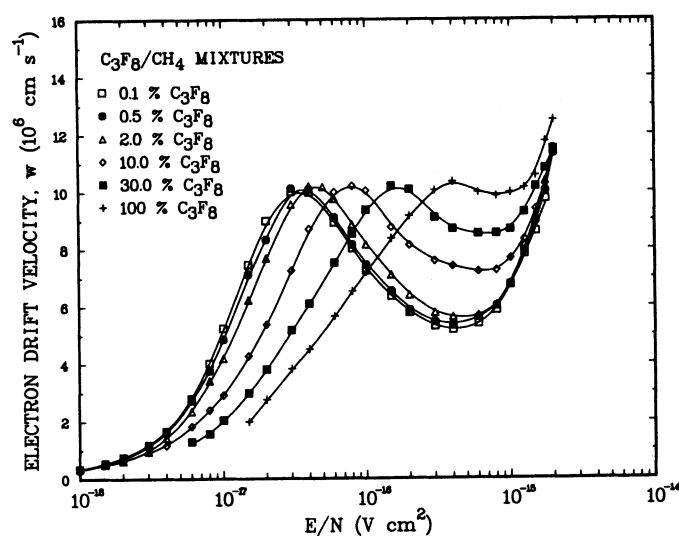
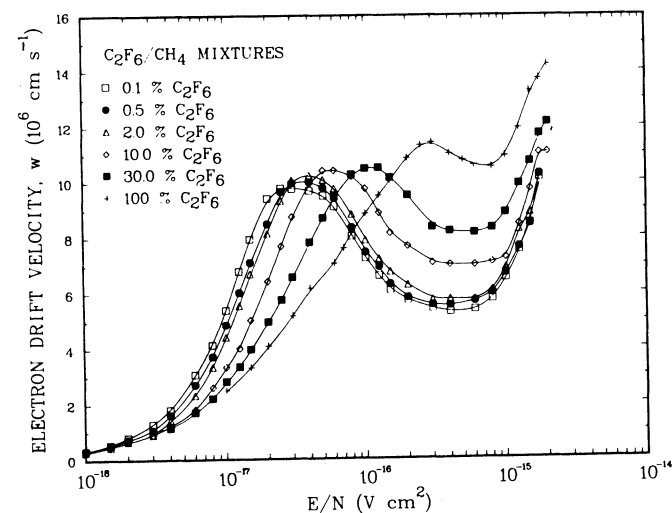
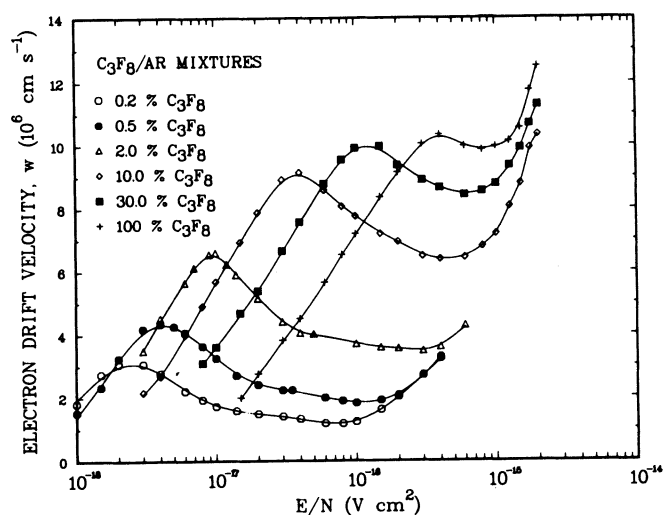
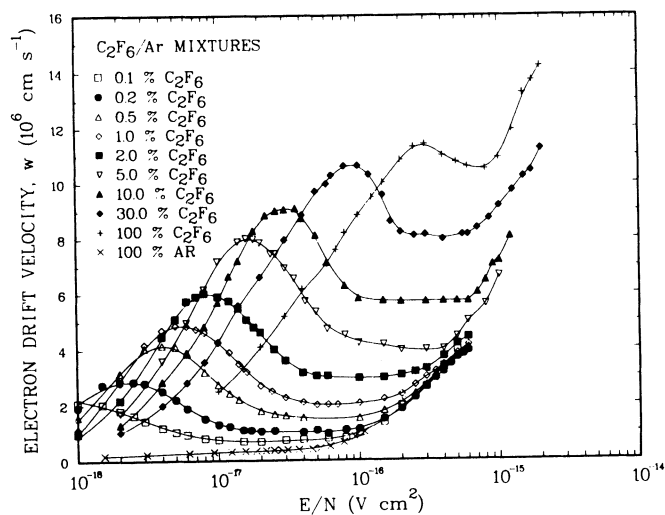


Fig. 20: w versus E/N for C₂F₆/Ar and C₂F₆/CH₄ mixtures [6,72,73].

Fig. 21: w versus E/N for C₃F₈/Ar and C₃F₈/CH₄ mixtures [6,72,73].

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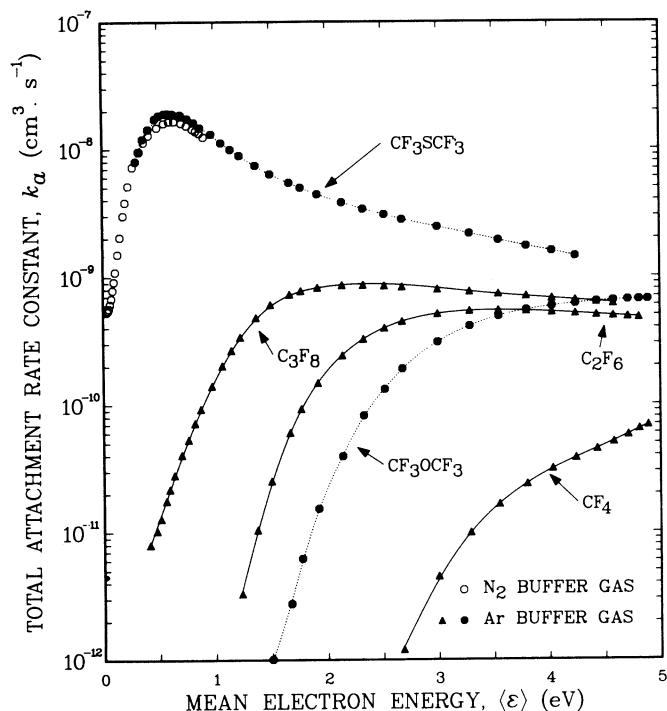


Fig. 22: Swarm determined total electron attachment rate constants as a function of the mean electron energy $\langle \epsilon \rangle$ for CF_4 , C_2F_6 , C_3F_8 , CF_3OCF_3 and CF_3SCF_3 . These were independent of both the attaching and the buffer gas pressure [6,72].

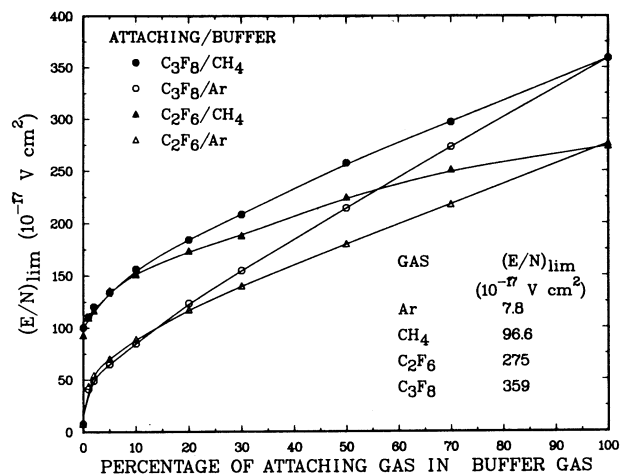


Fig. 23: $(E/N)_{lim}$ for C_3F_8 or C_2F_6 in Ar or CH_4 [Refs. 6, 72].

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