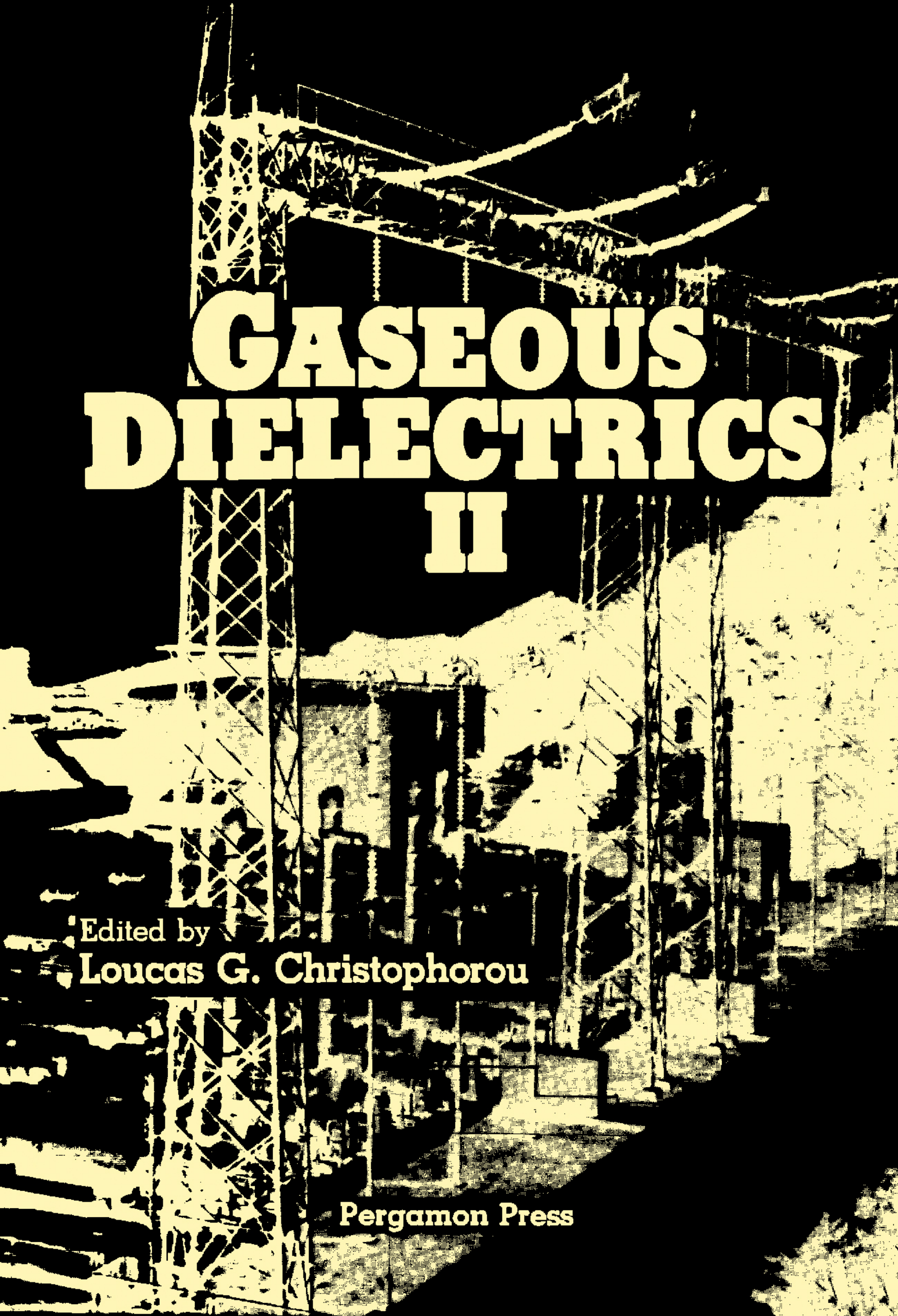

GASEOUS DIELECTRICS
II

Edited by
Loucas G. Christophorou

Pergamon Press

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Knoxville, Tennessee, U.S.A.
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PREFACE

The First International Symposium on Gaseous Dielectrics was held in Knoxville, Tennessee, on March 6-8, 1978. It brought together leading individuals from universities, research laboratories, industrial centers, utilities and funding agencies from throughout the world, interested in gaseous dielectrics.

The Second International Symposium on Gaseous Dielectrics was held two years later, again in Knoxville, Tennessee, on March 9-13, 1980. It provided a similar international forum for (i) a report on and a discussion of the current progress and problems in gaseous dielectrics and the effective use of gas dielectrics by the electric power industry, and (ii) a planning for a comprehensive and well-balanced future for research in, and development and utilization of, gaseous dielectrics.

The success of these international forums to bring together, perhaps for the first time, individuals interested in virtually all aspects of gaseous dielectrics, reinforced considerably the underlying unity of their complementary tasks. This development and the wholistic approach to the entire field of gaseous dielectrics—embracing its basic, applied, developmental and industrial aspects—adopted in these meetings, are in themselves a distinct achievement. They constitute a source of optimism for a well-balanced future growth in basic research and development, and in the industrial utilization of gaseous dielectrics.

In the intervening two years between the two symposia, many advances have been made both in the basic and applied areas and in the industrial sector. The presentations and discussions in this volume give ample description of these developments. A most distinct advancement in this period, also, has been the maturing of the realization of the great potential of gaseous dielectrics in the many and varied needs of the electric power industry, and in energy conservation.

The International Organizing Committee of the Second International Symposium on Gaseous Dielectrics consisted of: L. G. Christophorou (U.S.A.) (Chairman), D. W. Bouldin (U.S.A.) (Secretary), O. Farish (U.K.), T. F. Garrity (U.S.A.), T. Nitta (Japan), R. Samm (U.S.A.) and W. Zaengl (Switzerland). The local arrangements committee consisted of members of the Atomic, Molecular and High Voltage Physics Group and personnel of the Conference Office of Oak Ridge National Laboratory. To each member of these committees a deep depth of gratitude is due for invaluable contributions and unselfish help.

The Symposium was sponsored by the Oak Ridge National Laboratory and the U.S. Department of Energy, and was organized in cooperation with the Electric Power Research Institute, the Institute of Electrical and Electronics Engineers, Inc. and its Power Engineering Society. The financial and moral support of the sponsors is gratefully acknowledged.

Finally, I wish to thank innumerable colleagues for valuable advice.

Loucas G. Christophorou
Oak Ridge, Tennessee, May 1980.

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GASEOUS DIELECTRICS
II

IONIC AND ELECTRONIC PROCESSES IN SULFUR HEXAFLUORIDE

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ABSTRACT

Ion mobility and volume recombination coefficient in SF_6 were measured in the pressure range 10 mbar to 21 bar. The mobilities of positive and negative ions were found to be approximately equal. Below 1 bar the mobility varied with pressure as p^{-1} while above 1 bar a $p^{-1.25}$ dependence was observed. The recombination coefficient at high pressures exhibited the same $p^{-1.25}$ dependence while at low pressures a pressure proportional increase was measured. These results are discussed in the frame work of current mobility and recombination theories.

Charge multiplication measurements under pre-breakdown conditions revealed the influence of p on the multiplication process.

INTRODUCTION

Sulfur hexafluoride has obtained great importance as an insulating medium in high voltage equipment. Its dielectric strength at 1 bar is more than twice the value of air and in cables and switches operating pressures of several bar are employed. This allows the design of compact installations with higher voltage levels than open air installations of similar size.

The breakdown properties of SF_6 under various conditions have received considerable attention and the influence of electrode roughness, electrode geometry, purity of the gas etc. on the breakdown process has been investigated in great detail [cf. 1]. Most of these studies were initiated from a technical point of view.

Parallel to these technically-oriented studies the basic physical conduction phenomena in SF_6 were investigated. Quantities measured were ion mobilities [2-7], recombination coefficients [8], Townsend ionization coefficients and electron attachment rates [9-12].

Due to experimental difficulties these studies were carried out at low pressures ranging from several mbar to several hundred mbar. Extrapolation of the results to higher pressures and application of these data to the solution of problems encountered in the technological pressure interval remained ambiguous.

It seemed desirable, therefore, to extend the range of fundamental investigations to higher pressures in order to provide more realistic fundamental data on the conduction phenomena in SF_6.

Since many years in this laboratory a method for the injection of excess charge carriers into insulators has been successfully employed for the investigation of the electronic transport properties of non-polar liquids [13]. Charge carriers are produced by irradiating the material with a short flash of nanosecond duration of high-energy bremsstrahlung from a 15 MeV linear electron accelerator. The penetrating power of these x-rays is very large and homogeneous ionization can be produced in samples contained in thick wall test vessels. The short duration of the excitation pulse allows the study of fast phenomena [14, 15].

Recently we applied this technique to the investigation of ionic processes in compressed SF_6 and N_2O [16, 17] and here a progress report is given of our work on sulfur hexafluoride. Ion mobility and recombination were studied as a function of pressure, temperature and electric field strength. Charge carrier multiplication was investigated in the prebreakdown region.

During the course of the study it became evident also that measurements at pressures below one atmosphere would be desirable for comparison. Data obtained in rarefied SF_6 are included in this report.

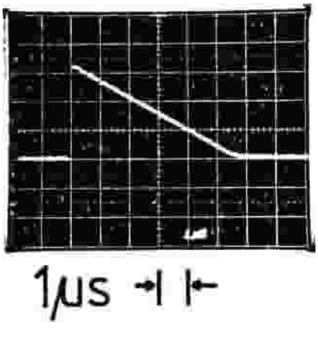


Fig.1 - Oscilloscopic trace of drift experiment; p = 1,1bar; U=23kV; d=0,32cm

EXPERIMENTAL

Samples and Cells

The sulfur hexafluoride used in these experiments was supplied by Messer Griesheim G.m.b.H.. It has a stated purity of > 99.9 vol% with the main impurities being air $\leqslant$500 vpm, CF_4 $\leqslant$500vpm, H_2O $\leqslant$15 vpm, and HF $\leqslant$1 vpm. Most of the measurements were performed without further purification of the gas. In some experiments gas was used which had been passed through a cold trap maintained at dry ice temperature. No influence of this treatment on the data was found.

Several measurement cells were constructed, which differed from each other by the maximum permissible value of voltage, pressure, temperature, and gap separations. The cell body was made of stainless steel with ceramic insulators for the electrical connections. The high voltage electrode consisted of a circular disk with a rounded contour. The circular ground electrode was surrounded by a guard ring in order to provide a defined measurement volume of constant electric field strength. For the charge multiplication experiments also electrodes with Bruce profile [18] were used.

Mobility measurement

The gas between the parallel electrodes was irradiated with a short pulse of x-rays and the decay of the ionization current due to drift of the charge carriers to the electrodes was monitored in time. A typical oscilloscopic trace is shown in Fig. 1. Usually 10^7 to 10^8 charge carrier pairs per cm^3 were generated by one x-ray pulse. The strict linearity of the decay is an indication that no recombination losses occurred during the drift, that space charge effects due to gross charge separation were negligible, and that the mobilities of positive and negative ions were equal. The drift time t_D was read directly from the oscilloscopic trace. The mobility μ is then given by

$$\mu = \frac{v_D}{F} = \frac{d^2}{t_D U} \qquad (1)$$

where d is the electrode separation and U is the applied voltage, $F = U/d$ and $v_D = \frac{d}{t_D}$.

Recombination measurement

The volume recombination coefficient k_r was determined by measuring the total charge which remained in the volume V at time t_r after the x-ray pulse. At t_r a high voltage pulse was applied to the cell which swept out the remaining charge carriers. The charge $Q(t_r)$ was measured with a Keithley model 602 electrometer.

Plotting $Q(t_r)$ as

$$Q(t_r)^{-1} = Q(o)^{-1} + \frac{k_r}{eV} \cdot t_r \qquad (2)$$

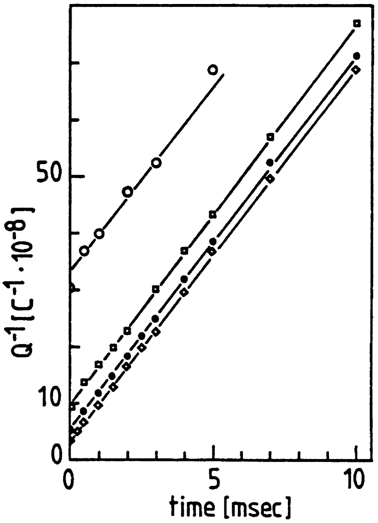


Fig. 2 - Collected charge Q as a function of the recombination time t_r. Four different initial charges Q(o).

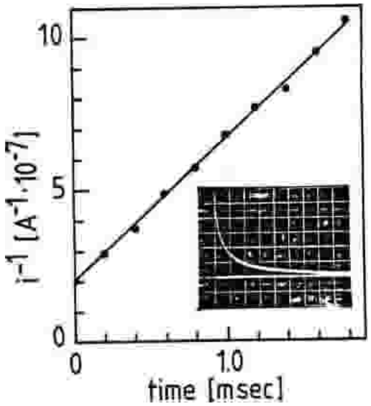
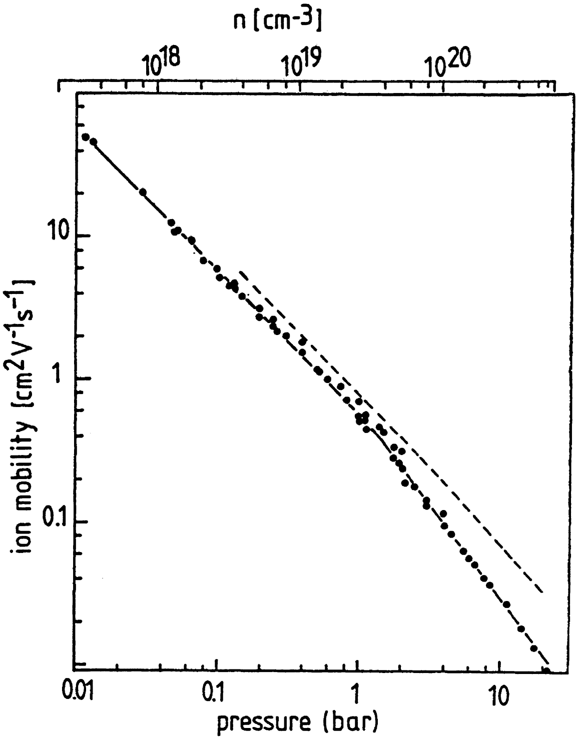


Fig. 3 - Decay of the ionization current after an intense pulse of x-rays; U = 20 V; d = 0.5cm; p = 4bar.



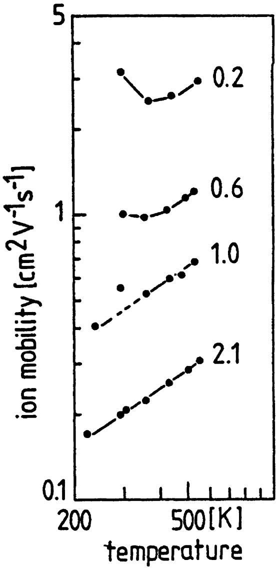


Fig.5 - Temperature dependence of ion mobility; parameter pressure in bar at T = 296K.

Fig.4 - Ion mobility as a function of pressure at T = 296K; dashed line calculated values according to Langevin theory.

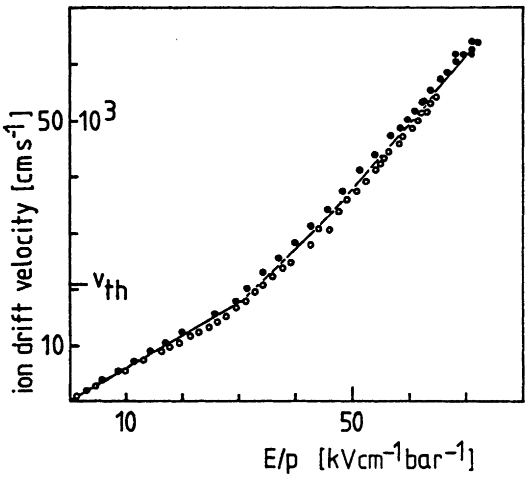


Fig.6 - Ion drift velocity as a function of E/p at T = 296K for p = 1.1 bar (●), and p = 1.98 bar (o).

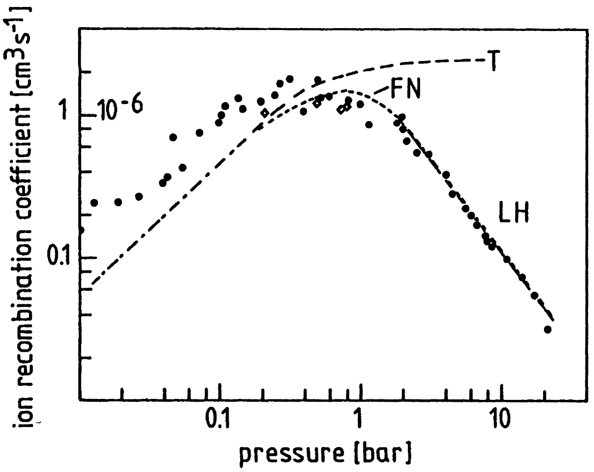


Fig.7 -Volume recombination coefficient as a function of pressure at T = 296K. Each point is the average of 2 to 4 measurements.

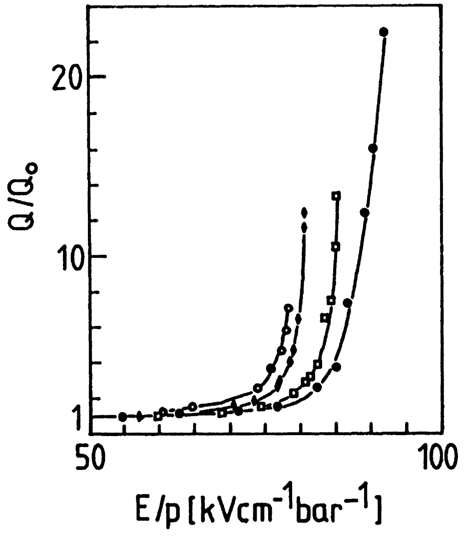


Fig.8 - Charge carrier multiplication in SF_6 at T = 296K ● 0.17bar, ☐ 0.37bar, ♦ 0.74bar, o 1.5bar

yielded a straight line from which k_r could be obtained (cf.Fig.2).

In compressed SF_6 for comparison we also observed the decay of the ionization current after an intensive pulse of x-rays. At low applied voltages recombination is the predominant process of carrier removal and the time dependence of the ionization current is given by

$$i(t)^{-1} = i(o)^{-1} + \\ + \frac{k_r}{e(\mu_+ + \mu_-)} \frac{d}{U\cdot q} t \qquad (3)$$

(q = electrode area)

In Fig.3 an example of a decay curve and its evaluation according to eq.3 is shown. Determination of k_r requires knowledge of $\mu_\pm$. The k_r-values obtained with this method agreed within experimental error with the data from the clearing field method. Fig.7 contains clearing field data only.

Charge multiplication

A voltage was applied to the cell and the charge produced by a constant pulse of x-rays was measured either directly with an electrometer or by integrating the oscilloscopic trace of the ionization current. At low values of E/p saturation of the collected charge was observed and for higher values of E/p multiplication factors were obtained by relating the observed charge Q to the charge Q_0 under conditions of saturation.

RESULTS

At low electric field strength the drift velocity v_D was found to be proportional to the field strength E and the low field mobility as a function of the gas pressure is shown in Fig.4. At pressures below 1 bar the mobility is inversely proportional to p^{-1} while above 1 bar a $\mu \propto p^{-1.25}$ dependence is observed. The temperature dependence of the ion mobility is shown in Fig.5. The cell was filled at room temperature with the pressure given in the figure. The temperature coefficient is positive and $\mu \propto T^{0.7}$ was found. The variation of the ion drift velocity as a function of the applied field strength is given in Fig.6. While below 32kV $cm^{-1}bar^{-1}$ v_D is proportional to E/p at higher values of E/p a stronger increase of v_D is observed.

The volume recombination coefficient k_r as a function of pressure is shown in Fig.7. At low gas pressures k_r was found to increase proportional to p, at intermediate pressures a broad maximum is observed, while at higher pressures k_r decreases inversely proportional to $p^{-1.25}$. The only other data available in the literature by Wilson et al. [8] are included for comparison.

Charge multiplication factors obtained at four different pressures below and above 1 bar as a function of E/p are shown in Fig.8.

DISCUSSION

Generation of ions in SF_6 by high energy x-rays proceeds via ionization, dissociation and electron attachment

$$SF_6 \rightsquigarrow SF_6^+ + e^- \qquad \text{(I)}$$

$$SF_6^+ \longrightarrow SF_5^+ + F \qquad \text{(II)}$$

$$e^- + SF_6 \longrightarrow SF_6^- \qquad \text{(IIIa)}$$

$$e^- + SF_6 \longrightarrow SF_5^- + F \qquad \text{(IIIb)}$$

These ions may react with neutral molecules to form e.g. $SF_6^-(SF_6)_2$ etc.[7]. In our experiments ions with only one mobility were observed and we conclude that $\mu_+ \approx \mu_-$. We have to point out, however, that our method of mobility measurement does not allow the discrimination of ions with mobilities which differ less than 20 per cent from each other. In some experiments a second linear decay could be inferred which led to a mobility approximately 20 per cent smaller than the value corresponding to the main linear decay. Since the variations of the mobility with pressure extended over several orders of magnitude no detailed analysis was attempted.

The theoretical descripton of ionic motion in gases has received continuous interest and several models have been developed [cf. 19]. Most of these studies treated the case of simple, mainly atomic ions in rare gases.

A theoretical description of the properties especially of parent ions in electronegative gases is not available. A comparison of existing theoretical transport models with our data, however, is quite elucidating. The most simple mobility mechanism is that proposed by Langevin (1903) [cf.21]. An ion is drifting under the influence of the electric field and it is suffering numerous elastic collisions with the gas molecules. The mobility is then approximately given by

$$\mu \approx \frac{e\,\lambda}{M\,v_{th}} \qquad (4a)$$

v_{th} is the thermal velocity of the gas molecules and of the ions since $M \approx M_i$; λ stands for the mean free path. At low pressures p it follows $\lambda \propto p^{-1}$ or since n (number density) is proportional to p we also have $\mu \propto n^{-1}$.

The temperature dependence of μ is determined by v_{th} which increases proportional to $\sqrt{T}$. Only at low pressures and low temperatures this behavior was indicated by the experimental data (Fig.5). At higher temperatures in all cases investigated $\mu \propto T^{0.7}$ was found.

Quantitatively eq.4a yields values which are too large. Better agreement with the data at T = 296K below 1 bar can be obtained with an improved mobility equation derived by Hasse [cf.21] in which some details of the ion-molecule scattering process have been included.

$$\mu_{LH} = \frac{A(\Lambda)}{\sqrt{\rho\,(\epsilon - 1)}} \sqrt{\left(1 + \frac{M}{M_i}\right)} \qquad (4b)$$

with ρ gas density, ϵ dielectric constant, M molecular mass, M_i ion mass. $A(\Lambda)$ is a function of the parameter Λ which is defined as

$$\Lambda^2 = \frac{8\pi\,p\,D_{12}^4}{(\epsilon - 1)\,e^2} \qquad (4c)$$

with p gas pressure, D_{12} sum of radii of ion and molecule, e elementary charge. Λ^2 is the ratio of thermal energy k_BT and the energy of polarization when ion and molecule are in contact. Evaluation of eq.4b and 4c with the molecular properties of SF_6 and tabulated values of $A(\Lambda)$ [cf.21] yielded values of $\mu_{LH} = 1.4\,\mu_{obs}$ (dashed line in Fig.4). At pressures above 1 bar the deviation increased.

It is generally recognized that in electronegative gases formation of labile cluster ions is an important process which influences the transport properties [cf.22]:

$$\begin{bmatrix} SF_6^- \\ SF_5^+ \end{bmatrix} + nSF_6 \rightleftharpoons \begin{bmatrix} (SF_6^-) \\ SF_5^+ \end{bmatrix} (SF_6)_n \qquad (IV)$$

$$\downarrow$$

$$\begin{bmatrix} (SF_6^-) \\ SF_5^+ \end{bmatrix} (SF_6)_m + (SF_6)_{n-m}$$

This process can be considered as an equilibrium which depends on the physical conditions (pressure, temperature, electric field etc.) of the gas.

Although Patterson [7] could identify with a mass spectrometer stable ion-clusters at low pressures, we believe that in the pressure range where our study has been carried out processes described by (IV) take place on a microscopic time scale leading to the macroscopic mobility. Further support for this hypothesis comes from the E/p dependence of the mobility. At ion drift velocities comparable to v_{th} (2.1×10^4 cm s^{-1}) at E/p ≈ 32 kV cm^{-1}bar^{-1} an overproportional increase of v_D with E/p is observed. Increase of the mean ion energy either by temperature or by electric field leads to a shift of the equilibrium of (IV) to the left hand side.

Another mechanism which has an effect on the mobility is charge transfer

$$SF_6^- + SF_6 \longrightarrow SF_6 + SF_6^- \qquad (V)$$

since during the time of contact the mass M_i increases, thus decreasing the mobility. Wannier [cf.21] developed an ion mobility theory which took into account rigid sphere repulsion and symmetry forces (which characterize charge transfer). For high fields Wannier showed that the drift velocity should vary proportional to $\sqrt{E/p}$, which was not observed in our experiments (cf.Fig.6).

More sophisticated mobility theories require a detailed knowledge of the ion-molecule interaction potential (cf.19].

The mechanism of ion recombination depends on the pressure. At very low pressures two body recombination

$$M^+ + M^- \xrightarrow[k_b]{} M_2^*(\text{excited}) \qquad (VI)$$

is the prevailing process. The recombination coefficient k_b is very small (for instance ≈ 10^{-8}cm^{3}s^{-1} for oxygen [cf.20]). As the pressure is increased an increase of the recombination coefficient is observed due to participation of a neutral molecule in the recombination process, which absorbs the excess energy

$$M^+ + M^- + M \xrightarrow[k_T]{} 3M \qquad (VII)$$

This case has been analyzed theoretically by J.J.Thomson [cf.21]. The recombination coefficient is given by

$$k_T = \pi r_1^2 (v_{M+}^2 + v_{M-}^2)^{1/2} \Big[1 - \frac{\lambda_i^+}{2r_1}\left(1 - e^{-2r_1/\lambda_i^+}\right) + 1 - \frac{\lambda_i^-}{2r_1}\left(1 - e^{\frac{2r_1}{\lambda_i^-}}\right)\Big] \qquad (5a)$$

Here $r_1 = \frac{2e^2}{3k_B T}$ is the critical distance where the thermal energy is equal to the Coulomb energy of attraction, $v_{M\mp}^{\pm} = \sqrt{\frac{8k_B T}{\pi M_\pm}}$ denotes the mean thermal velocity of the ions,
$\lambda_i^\pm$ is the mean free path of the ions.

Values of $\lambda_i^{\pm}$ can be obtained from the mobility data via [cf.23]

$$\lambda_i^{\pm} = \frac{16}{3e} \left(\frac{M_r^{\pm} k_B T}{2} \right)^{1/2} \mu_{\pm} \qquad (5b)$$

with M_r the reduced mass given by $M_r^{-1} = M_i^{-1} + M^{-1}$.

Values for k_T were calculated and the results are included in Fig.7. The theoretical values are too low by a factor of two. The general dependence on pressure is, however, represented quite well.

At high pressures the recombination coefficient decreases with increasing pressure. The rate determining step is the mobility of the ions.

Langevin and Harper [cf.21] found proportionality between k and μ

$$k_{LH} = 4\pi e(\mu_+ + \mu_-) \qquad (6)$$

Comparison of the mobility values of Fig.4 with the recombination data of Fig.7 shows the required proportionality; also quantitative agreement is obtained.

Ion recombination in the intermediate pressure interval was treated theoretically by Natanson [cf.23] who combined the Thomson model with the Langevin-Harper model. The formula for the recombination coefficient k_N is somewhat complex. Numerical calculations were performed and the results are also included in Fig.7. At low pressures k_N follows k_T while at high pressures k_N goes over into k_{LH}. The discrepancy of k_T and the experimental data at low pressure may be caused partially by the method of measurement employed here. Recombination measurements require high initial charge carrier concentrations which are difficult to generate at low pressures. Data taken at different absorbed doses showed the influence of initial ion concentration. The values given in Fig.7 are thought to represent our best data on homogeneous volume recombination.

Charge carrier multiplication as measured as a function of E/p is shown in Fig.8. With increasing pressure the onset of multiplication is shifted to lower values of E/p. At the same time a steeper increase of Q/Q_0 with E/p and smaller obtainable values of Q/Q_0 were observed. Further increase of E even by as small as 1 per cent yielded breakdown of the gap.

Charge carrier multiplication in an electronegative gas is thought to proceed via a Townsend mechanism with an effective ionization coefficient $\bar{\alpha}$ determined by the simultaneous action of ionization (α) and attachment (η). The number of charge carrier N produced in a gas of pressure p under the action of an electric field E for an initial number N_0 generated at the cathode was calculated by Harrison and Geballe [10].

$$\frac{I}{I_0} = \frac{N}{N_0} = \left\{ \frac{\alpha}{\alpha-\eta} \exp[(\alpha-\eta)d] - \frac{\eta}{\alpha-\eta} \right\} \qquad (7)$$

Integration of eq.7 over d yields the multiplication factor for the case of volume ionization as employed in our experiments

$$\frac{N}{N_o} = \frac{1}{d}\left\{ \frac{\alpha}{(\alpha-\eta)^2}\left[e^{(\alpha-\eta)d} - 1\right] - \frac{\eta d}{\alpha-\eta} \right\} \qquad (8)$$

N/N_0 is strongly dependent on $(\alpha-\eta)d$. Bhalla and Craggs [9] measured $\alpha(E/p)$ and $\eta(E/p)$ for E/p = 85 V $cm^{-1}torr^{-1}$ and E/p = 150 V cm^{-1} $torr^{-1}$. There was no influence of the pressure between 5 and 100 torr. If we calculate N/N_0 as a function of E/p according to eq.8 we find a much smaller dependence on p at fixed electrode separation than observed experimentally.

Tentatively one may assume that at higher pressures either $\alpha(E/p)$ and $\eta(E/p)$ depend on the pressure or/and that collisional detachment of electrons from negative ions leads to an apparent decrease of η.

Further experiments also at higher temperatures should shed more light on this problem.

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K. SIOMOS: If the break in the log P vs log I plot were due to energy loss via collisions, wouldn't you expect to see a different than linear behavior after the break? Did you do any temperature experiments? These experiments would be very effective in testing the "clustering" assumption. How do you explain your results in Fig. 5 with the Langevin equation?

W. F. SCHMIDT: The break occurs when the kinetic energy associated with the drift becomes comparable to the thermal energy kT. The clusters break up more often. Increase of temperature (Fig. 5) yields the same result. Langevin's theory would predict a decrease of the mobility with increasing temperature. The theory does not take into account the effect of labile clusters on the mobility.

R. J. VAN BRUNT: You mentioned that the mobilities of the positive and negative ions were observed to be the same. Is this also the case at pressures above about 1 bar where it was mentioned that ion clustering for negative ions is expected to occur, i,e., does clustering also occur for positive ions?

W. F. SCHMIDT: Also at higher pressures ($P > 1$ bar) we observed that positive and negative ions exhibit the same mobility. Clustering is assumed to occur with the positive ions as well.

M. MISAKIAN: I wish to introduce into the discussion a reference by Patterson [J. Chem. Phys. 53, 696 (1970)] in which measurement of negative ion mobilities in SF_6 are made using an apparatus incorporating time-of-flight and mass analysis. Four ionic species are identified: SF_5^-, SF_6^-, $SF_6^-(SF_6)$, and $SF_6^-(SF_6)_2$. A sparking wire was used as the ion source with gas densities 1 to 14 x 10^{16}cm^{-3}. Measurements of the mobilities as a function of E/N are presented and it would be of interest to compare the Patterson results with your data.

W. F. SCHMIDT: There is some argument in the literature if in such an experiment the ions observed in the mass analyzer are the same as those observed in the drift tube. Patterson reported four types of mobilities ranging from approximately 0.46 cm^{2}V^{-1}s^{-1} to 0.56 cm^{2}V^{-1}s^{-1} at 760 torr which he attributed to SF_6^-, SF_5^+, and some clustered ions. Our values at 760 torr fall right into this interval. However, we do not wish to draw any conclusion as to the identity of our ions by a closer comparison of their mobility with Patterson's data.

CALCULATION OF ELECTRIC FIELD-INDUCED DETACHMENT RATE OF ELECTRONS FROM MONONEGATIVE IONS; RELEVANCE TO GASEOUS DIELECTRICS*

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ABSTRACT

Our model for the mononegative atomic or molecular ion in its effect on the most loosely bound electron is a "spherical square well" (constant positive inner potential within a sphere of radius r_o and zero potential outside). From it we have calculated by quantum mechanics the emission rate $w_{\nu\ell m}$ of electrons from the ν^{th} excited state (of orbital angular momentum and magnetic quantum numbers ℓ and m and energy $E_{\nu\ell} < 0$) under the influence of a constant electric field F. The calculation is conceptionally simple (involving time-dependent perturbation theory) but technically complicated (requiring an eleven-fold integration), and leads to a surprisingly simple final expression. The relevance of our calculations to gaseous dielectrics is discussed.

INTRODUCTION

We have repeatedly pointed out earlier (e.g., see Ref. 1) that the most desirable way of removing electrons from an electrically stressed gaseous dielectric—in order to effect a higher dielectric strength—is capture of the electrons by the dielectric gas molecules forming negative ions. These ions diffuse to the walls of the container and are destroyed there. If, however, the electrons are loosely bound to the atom, radical, or molecule (i.e., if the electron affinity, EA, of the capturing species is small, say, close to 3/2 kT), the ions, A^-, can be efficiently destroyed in collisions with neutral species (via the processes of associative and nonassociative collisional detachment) and/or by electric fields (field-induced electron detachment) when the latter are large. It is of course possible that other electron detachment processes (e.g., photodetachment, electron impact-induced detachment; see Chap. 7 of Ref. 2 and Discussion) can occur. 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

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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. 3-5, 4-8 and 9, respectively). Constant uniform electric fields of the order of 100 kV/cm and 2 MV/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 (Ref. 2, Chap. 7).

In this paper we estimate 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 static electric field as a function of the angular momentum quantum number, ℓ, the magnetic quantum number, m, the EA, and the size of the anion. We also discuss the implications of the obtained results to gaseous dielectrics.

ELECTRIC FIELD-INDUCED DETACHMENT OF AN ELECTRON FROM A MONONEGATIVE ION

In this section a calculation is presented of 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 static electric field. We choose singly charged ions to insure that the interaction between electron and residual atom or molecule at large separations is weaker than the Coulomb interaction. We assume that the applied electric field is uniform and weak compared to the atomic field.* The transition probability per unit time is, then, small compared to the atomic unit of transition probability per unit time. These assumptions imply that the electron becomes free by tunneling through a potential barrier of appreciable size.

The wave function $\psi_{o\ell m}$ of the most weakly bound electron is assumed to feel no force for $r \geq r_o$, where r_o is the radius of a sphere which contains all save a small fraction f_ℓ of this most weakly bound electron's charge. The energy of this electron is negative, equal to $E_{o\ell} = -(EA)$. The wave function for $r > r_o$ then satisfies $-(\hbar^2/2m)\nabla^2 \psi_{o\ell m} = E_{o\ell}\, \psi_{o\ell m}$, where ∇^2 is Laplace's operator. We shall also write $-(EA) = -\hbar^2\kappa^2/2m$ to get the simplified equation $\nabla^2 \psi_{o\ell m} = \kappa^2 \psi_{o\ell m}$ for the outer part of the wave function. We shall need none of the details of the wave function or potential energy for $r < r_o$ except that the energy is $-(EA)$ and that the solutions have the transformation properties of the spherical harmonics $Y_{\ell m}(\theta,\phi)$ and are properly continuous with continuous radial derivative at $r = r_o$.

Solutions to the scalar Helmholtz equation with imaginary wave vector are well-known. Choosing those which vanish exponentially as $r \to \infty$, we have

$$\psi_{o\ell m}(r,\theta,\phi) = c_{o\ell}\, h_\ell^{(1)}(i\kappa r) Y_{\ell m}(\theta,\phi),$$

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*In the following, $-e$ and m are the charge and mass of the electron, $\hbar = h/2\pi$ (where h is Planck's constant), and c is the speed of light. The unit of length is the radius of the first Bohr orbit, $a_H = \hbar^2/me^2 \cong 0.53 \times 10^{-8}$ cm; the unit of energy is the Rydberg, $e^2/2a_H \cong 13.6$ eV; the unit of electric field is the atomic field, $e/a_H{}^2 \cong 5 \times 10^9$ volt cm^{-1}; and the unit of transition probability is $(e^2/2a_H)/\hbar \cong 2 \times 10^{16}$ sec^{-1}.