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Simultaneous Measurement of Ionization and Attachment Coefficients*

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Measurements have been made of pre-breakdown currents in four gases: oxygen, air, freon-12 (CCl_2F_2), and CF_3SF_5. The behavior of these currents differs from that previously attributed to all gases in that semilogarithmic graphs of current against electrode separation at constant E/p exhibit initial curvature, being concave toward the electrode separation axis. At low E/p an apparent saturation is found. This behavior is interpreted as resulting from a reaction of dissociative attachment of the kind $AB+e=(AB^-)^*=A+B^-$. On this basis simultaneously determined values of the ionization and attachment coefficients can be deduced. In oxygen and air these parameters, when determined from separate experiments, show a somewhat anomalous behavior. The apparent anomalies are explained with the result that ionization is found to commence at lower, and attachment persist to higher values of E/p than previously suspected. In freon-12 and CF_3SF_5 it is found that the ionization coefficient is about an order of magnitude larger than reported for similar gases when no account is taken of possible attachment. The attachment coefficient is observed to be larger for halogen-containing molecules than for the same halogens when free. Cross sections for attachment are computed for oxygen and air. Dependence of the cross sections on mean electron energy is discussed with reference to energy scales in these two gases.

INTRODUCTION

We have reported previously[1] on simultaneous measurements of the ionization and attachment coefficients in oxygen. Since that time two additional papers[2,3] describing measurements of attachment in oxygen have appeared, and we have extended our procedure to air, CCl_2F_2 (freon-12), and CF_3SF_5. It is the purpose of this paper to relate in more detail the method we have employed, to present our results in these gases, and to discuss these results in comparison with those of other workers.

Following Townsend[4] it has been generally assumed that the current in a pre-breakdown discharge between plane parallel electrodes is described for sufficiently small electrode separation by the familiar equation,

$$i=i_0e^{\alpha d}, \tag{1}$$

where i is the total current, i_0 the initial electron current at the cathode, d the electrode separation. The ionization coefficient α is the mean number of ionizations per cm in the field direction produced by electron collision. Although in complex gases more than one type of ionizing process may occur, no attempt has been made as yet to separate out the corresponding contributions to α. At large separations, as is well known,[5] significant deviations from Eq. (1) are observed. These are explained in terms of secondary ionizing processes which take place at the cathode or within the body of the gas. Such processes cause a more rapid increase of current with electrode separation than is indicated by Eq. (1) and are essential to the occurrence of breakdown.

In complex gases and in those containing electronegative atoms other reactions result from electron collision. Ions which are produced in such processes affect the density of current carriers in a manner quite different from the ionization processes described above. Many types of ion-producing reactions have been observed, principally through the use of mass spectrographs. At present we confine ourselves to three,

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* Supported in part by the U. S. Office of Ordnance Research.

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[1] R. Geballe and M. A. Harrison, Phys. Rev. 85, 372 (1952).

[2] A. Doehring, Z. Naturforsch. 7a, 253 (1952).

[3] P. Herreng, Cahiers phys. 38, 7 (1952).

[4] J. S. Townsend, Nature 62, 340 (1900).

[5] L. B. Loeb, *Fundamental Processes of Electrical Discharge in Gases* (John Wiley and Sons, Inc., New York, 1939), Chap. IX.

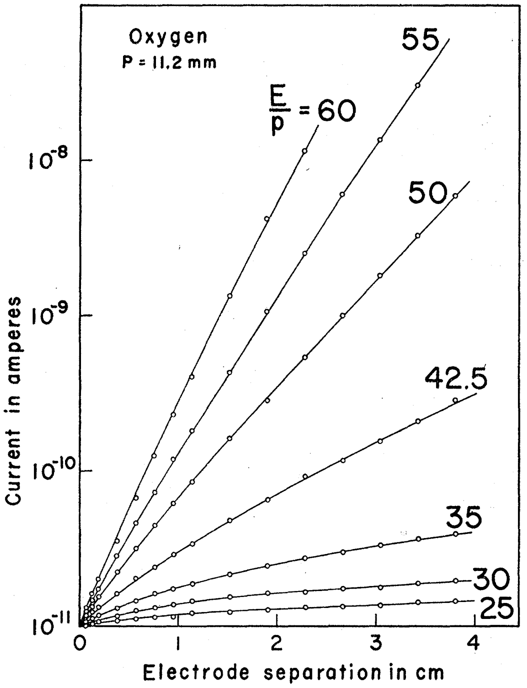

FIG. 1. Typical variation of ln$i$ with d in oxygen at 11.2 mm pressure. Each curve gives the results of a run at constant E/p. Data are normalized to the same i_0. Solid curves are drawn from Eq. (5).

designated as follows:

(A) Direct attachment, $AB+e=AB^-$.

(B) Dissociative attachment, $AB+e=(AB^-)^*=A+B^-$.

(C) Dissociation into ions, $AB+e=A^++B^-+e$.

We assume that at a given value of mean electron energy, characterized by the experimental parameter E/p, where E is the field strength in volts/cm and p the pressure in mm of mercury, one of the reactions predominates and the others can be neglected. Furthermore we permit only those electrode separations which are small enough that secondary ionizing processes of the kind leading to breakdown have no appreciable effect. Focusing our attention on reactions of the types A and B, we describe the attachment process by a parameter η which we define in analogy to α as the mean number of attachments per cm of drift in the field direction. In order to find the current which flows when this process and ionization by collision occur simultaneously, we make use of equations of continuity as follows:

$$\partial n_e/\partial t+v_e\partial n_e/\partial x=\alpha v_e n_e-\eta v_e n_e, \tag{2}$$

$$\partial n_+/\partial t+v_+\partial n_+/\partial x=\alpha v_e n_e, \tag{3}$$

$$\partial n_-/\partial t+v_-\partial n_-/\partial x=\eta v_e n_e. \tag{4}$$

In these equations the subscripts e, $+$, and $-$ refer, respectively, to electrons, positive ions, and negative ions, while n means numerical density, and v stands for drift speed in the gas. The steady-state solution for the total current, with suitable boundary conditions, is found to be

$$i=i_0[\alpha/(\alpha-\eta)]\exp[(\alpha-\eta)d]-i_0\eta/(\alpha-\eta), \tag{5}$$

as previously given. When reaction C predominates, the appropriate equations have the solution

$$i=i_0[(\alpha+\lambda)/\alpha]\exp(\alpha d)-i_0\lambda/\alpha, \tag{6}$$

where λ is a coefficient describing the rate of reaction C in the same manner that η describes the rates of A and B. Solutions can be readily written down for situations in which reactions B and C occur together and in which secondary ionization processes described by the usual coefficient γ are present as well, but these are of no present concern.

Ordinarily α is measured by determining the slope of a semilogarithmic graph of i against d, on the assumption that Eq. (1) is correct.[4,6] Experimental evidence indicates that this is valid procedure for a large number of gases. It has also been applied to gases in which reactions of types A, B and C are known to occur.[7,8] Now semilogarithmic graphs of Eqs. (5) and (6) are distinctly nonlinear. However if α is much larger than η and/or λ, the deviation from linearity will be difficult

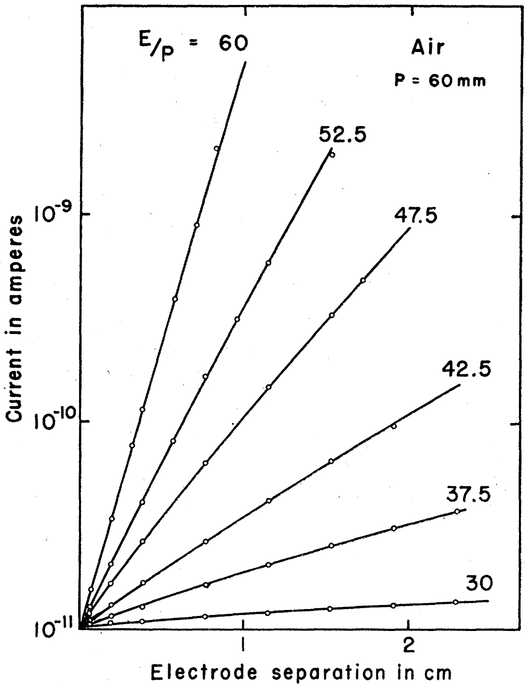

FIG. 2. Typical variation of ln$i$ with d in air at 60 mm pressure with normalized i_0. Solid curves are drawn from Eq. (5). Multiplication is much greater than in oxygen because of the smaller attachment rate.

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[6] Reference 5, Chap. VIII.

[7] B. M. Hochberg and E. J. Sandberg, Compt. rend. acad. sci. U.R.S.S. **53**, 511, (1946).

[8] K. Masch, Arch. Elektrotech. **26**, 587 (1932).

to observe. A similar difficulty occurs when the range of d is limited to large values, even if α is only slightly larger than η. In this event the additive terms in the equations are negligible, and the coefficient actually deduced will be $\alpha-\eta$. If d, because perhaps of instrumental limitations, is confined to small values (a few mm), the deviation again will be hardly apparent. The slope of a straight line drawn through the experimental points in this case will have no simple interpretation. It is apparent from this discussion that only if an extensive range of d is covered by experiment can the extent to which attachment and dissociation affect the discharge current be fully determined, and true values of the coefficients deduced.

APPARATUS AND PROCEDURE

The electrodes are polished copper disks 9 cm in diameter, with contoured edges. The anode is perforated at its center with about 400 holes within a circle of 2 cm diameter, and is rigidly mounted to the Pyrex vessel. A carefully made nut and screw with 40 threads per inch permit the cathode to be separated any distance between 0 and 4 cm through the agency of an iron armature which can be rotated by an external magnet. Ultraviolet light is admitted through a quartz window directly above the anode and falls normally on the cathode. The light intensity is monitored by a photocell; occasional adjustment of the load resistor is necessary to maintain sufficient constancy. The Pyrex vessel is made from a 5-liter flask and provides a minimum clearance of 4.5 cm. A coating of Dag on the interior wall of the vessel insures an equipotential boundary. Connection of this coating to a voltage divider permits adjustment of the wall potential. It was found possible to keep current diffusing to the wall less than 1 percent of the total even at the greatest electrode separation.

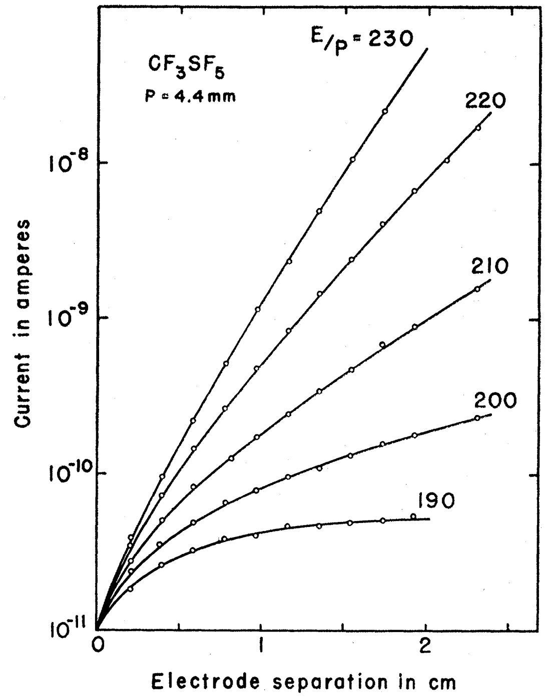

FIG. 4. Typical variation of ln$i$ with d in CF$_3$SF$_5$ at 4.4 mm pressure. Solid curves are drawn from Eq. (5). The saturation at low E/p is particularly apparent here.

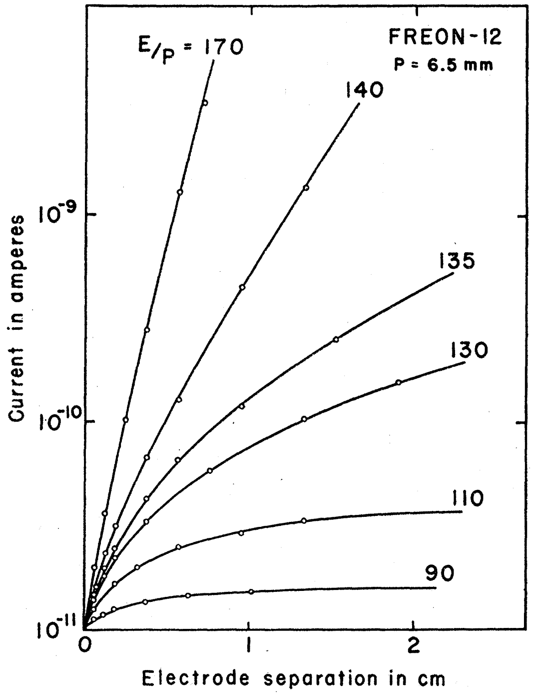

FIG. 3. Typical behavior of ln i in freon-12 at 6.5 mm pressure for various values of E/p. Solid curves are drawn from Eq. (5). Curvature is much more pronounced than in oxygen or air due to the very large attachment coefficient.

The vessel and electrodes have been thoroughly cleaned and baked at temperatures exceeding 400°C in vacuum and an atmosphere of hydrogen for several hours whenever it appeared desirable. Occasionally when either the electrodes became visibly coated or the initial photocurrent was found to be smaller than normal, the electrodes were removed and mechanically cleaned, and the baking process was repeated. The apparatus has not been used unless a pressure of less than 10^{-5} mm of mercury could be maintained for several hours in the closed-off vessel.

In order to be sure that the effects to be reported were not instrumental, measurements were also made in two gases, hydrogen and nitrogen, which are free of any reactions involving ions except ionization by collision.[9–14] Semilogarithmic graphs of current were

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[9] Mass spectrographic investigations have produced no evidence for the existence of N^- or N_2^- (see references 10 and 11). H^- has been reported in very small amounts (see references 12 to 14) but no estimates of the cross section for its formation are given. The present apparatus would have detected a process with a mean cross section of 10^{-21} cm^2.

[10] Tate, Smith, and Vaughan, Phys. Rev. **48**, 525 (1935).

[11] J. T. Tate and W. W. Lozier, Phys. Rev. **39**, 254 (1932).

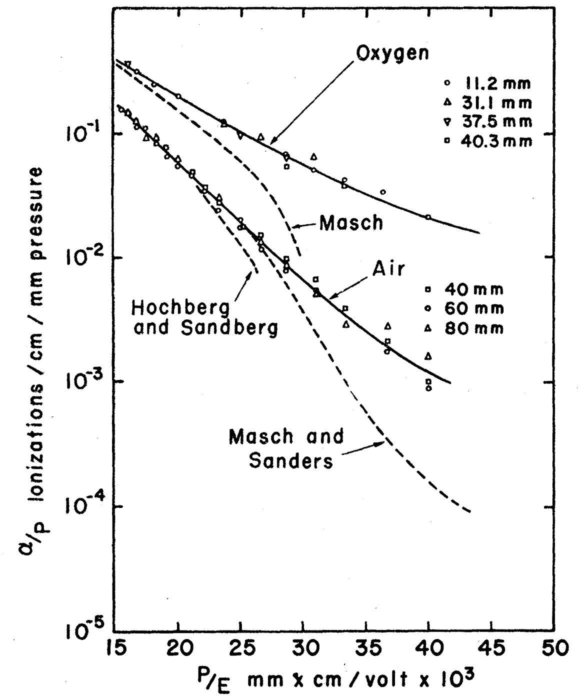

FIG. 5. Variation of ionization coefficient with p/E for oxygen and air. Solid curves are drawn by inspection through data of the present work. For a discussion of the other curves see text.

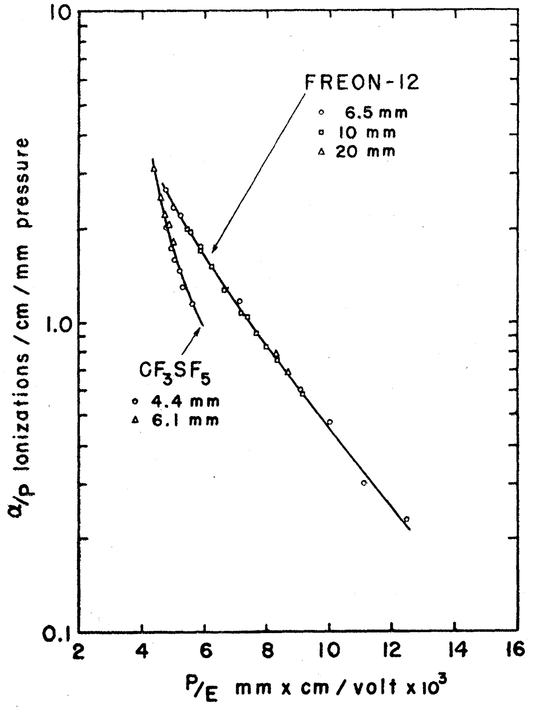

FIG. 6. Variation of ionization coefficient with p/E for freon-12 and CF_3SF_5. Solid curves are drawn by inspection through data of the present work. For discussion see the text.

linear within the accuracy of the measurements, except that under certain conditions a slight concavity to the electrode separation axis was noted at separations less than three turns of the screw. This effect was found as well when the photocurrent was measured in vacuum. Similar observations have been reported[15] and explained in terms of the reflection of light back up through the holes in the anode. The effect seems definitely correlated with the degree of parallelism of the electrodes; when they are visibly nonparallel, no concavity is observed for these gases. It has been found possible to correct for this effect, utilizing the results of vacuum measurements. The correction is about 3 percent at one turn, 1 percent at three turns.

Attempts were made to obtain considerable purity of all the gases used. Hydrogen was admitted through a palladium thimble, and in addition other samples of tank hydrogen were passed slowly over hot copper and through a liquid nitrogen trap. Behavior of hydrogen treated in these various ways was identical. Nitrogen for use in measurements was generated by decomposition of NaN_3, and was passed through a liquid nitrogen trap. Oxygen was produced in three ways: by decomposition of HgO, $KMnO_4$, and MnO_2, with suitable liquid nitrogen traps to remove impurities. Again no difference among them could be detected. Air from outside the laboratory was filtered through a plug of glass wool and passed through a liquid nitrogen trap. Freon came from a commercial cylinder and was distilled in vacuum several times before admission from a trap cooled to the temperature of liquid nitrogen. CF_3SF_5 obtained from the Department of Chemistry[16] was purified in the same manner as freon. Gas pressures were measured with a mercury manometer. During all manipulations except admission of the last two gases a liquid nitrogen trap served as protection against mercury contamination. Subsequent checks indicated that no detectable contamination was admitted in these latter operations. Samples of all gases were changed frequently. At no time was there evidence that a gas had altered its properties while measurements were being made.

High voltage was supplied by a regulated negative supply, and was read with a calibrated resistor and a potentiometer. Ionization currents were passed through one of a set of calibrated resistors which were frequently checked against each other. The potential drop across the resistor in use was read with a Dolezalek electrometer. Electrode separations were determined by counting revolutions of the screw. Current measurements were made for varying separations at constant E/p. The gas was never permitted to break down. At sufficiently large E/p, when the electrode separation was increased to more than about 2 cm, a conditioning of the cathode

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[12] W. W. Lozier, Phys. Rev. **36**, 1417 (1930).

[13] H. D. Smyth and D. W. Mueller, Phys. Rev. **43**, 116 (1936).

[14] O. Tüxen, Z. Physik **103**, 463 (1936).

[15] A. A. Kruithoff and F. M. Penning, Physica **3**, 515 (1936).

[16] Gene A. Silvey and George H. Cady, J. Am. Chem. Soc. **72**, 3624 (1950). We wish to thank Dr. Silvey and Professor Cady for supplying this compound.

surface appeared to take place which affected the initial photocurrent. To eliminate this effect, measurements in this range of E/p were carried out at either reduced pressure or reduced light intensity.

DATA

Samples of data obtained in the gases are shown in Figs. 1 to 4. The solid curves in these figures are computed from Eq. (5). By a careful curve-fitting procedure values of α and η can be found from each curve. The procedure fails when at low E/p it is found that $\eta \gg \alpha$, and the current hardly rises above i_0. At high E/p the magnitudes of η and α are reversed, the curvature is slight, and while α can be determined with considerable accuracy, η cannot.

It can be seen that a straight line drawn through the points for separations of greater than one cm will pass reasonably close to all of them, and the deviations could be taken for experimental scatter. A straight line could similarly be drawn through the points, say, between 0.2 and 0.8 cm. Neither of these gives the correct α in the region of E/p where detectable curvature exists.

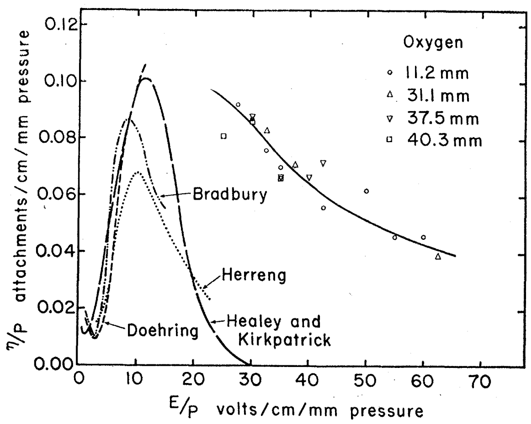

FIG. 7. Dependence of attachment coefficient on E/p for oxygen. Solid curve drawn by inspection through present data. Comparison data are given directly in reference 24 but have been computed from the results of references 2, 3, and 23 as discussed in the text.

Data of this nature were taken in oxygen at pressures (measured at 20°C) from 11.2 to 40.3 mm; in air, from 40 to 80 mm; in freon-12, from 6.5 to 20 mm; and in CF_3SF_5, at 4.4 and 6.1 mm. During a run at constant E/p individual points, particularly those at small separations, were repeated to check their reproducibility. In each gas the range of E/p extended throughout the region of applicability of the method for these pressures.

RESULTS AND DISCUSSION

1. Measurement of α/p and η/p

Several factors have led us to base our analysis of the curves on Eq. (5) rather than Eq. (6). Important among them is the apparent saturation exhibited by curves of Figs. 1 to 4. Such behavior is consistent only with the first of these equations. Furthermore in oxygen and in many complex gases it has been found that reactions of type B appear at electron energies of but a few volts,[17–20] whereas those of type C require more than ionization energy. Since dissociative attachment results from resonance capture of an electron, the cross section for this process can attain large values; e.g., a maximum of 10^{-16} cm^2 has been reported recently for SF_6.[20] Under conditions of the present experiments where ionization is just assuming a dominant role it seems quite unlikely that C should occur to an appreciable extent.

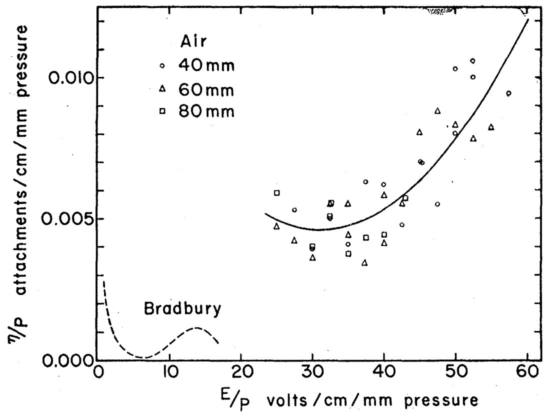

FIG. 8. Dependence of attachment coefficient on E/p for air. Solid curve again drawn by inspection. Scatter is greater than for oxygen, because of the smaller curvature in Fig. 2. Comparison curve computed from the results of reference 23. The considerable difference in magnitude has as yet no explanation.

On this basis Fig. 5 shows values of α/p found for oxygen and air plotted against p/E. This scale of

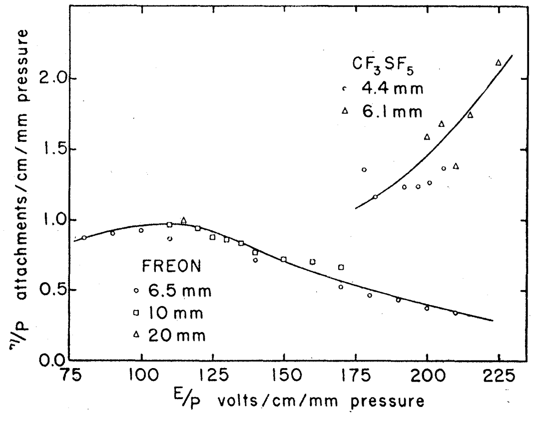

FIG. 9. Behavior of the attachment coefficient with E/p in freon-12 and CF_3SF_5. Curves are drawn by inspection. Scatter in the CF_3SF_5 is principally because these were the first data to be taken.

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[17] W. W. Lozier, Phys. Rev. **46**, 268, (1934).

[18] R. F. Baker and J. T. Tate, Phys. Rev. **52**, 683 (1938).

[19] R. H. Vought, Phys. Rev. **71**, 93 (1947).

[20] A. J. Ahearn and N. B. Hannay, J. Chem. Phys. **21**, 119 (1953).

abscissas is chosen because it produces for many gases a nearly linear graph. The solid curves are drawn by inspection. Included for comparison are results of other investigations.[8, 21, 22] It should be noted that the measurements of Masch[8] and of Hochberg and Sandberg[22] were made with separations between 0.2 and 0.8 cm, while Sanders'[21] did not extend below one cm. The first of these authors remarked on the probable effect of attachment on his oxygen data but did not analyze it. In air, where the effect of attachment is considerably diluted, curvature of the semilogarithmic graphs is slight for all E/p. Agreement between results of the quite different measurements of Masch and Sanders in this gas is readily accounted for by this circumstance.

There are no published data with which to compare the curves of Fig. 6 directly. Hochberg and Sandberg[7] have given values of α/p in several complex gases containing electronegative atoms, measured with separations of less than one cm. In agreement with their work and consistent with the high dielectric strength of such gases we find the net electron multiplication to be appreciable only at values of E/p considerably larger than for simple gases. The magnitude of α/p however is larger by about one order than reported by these authors.

Figure 7 shows the behavior of the attachment coefficient deduced for oxygen, reported in part previously.[1] Included for comparison are results of earlier investigations[23, 24] as well as two recent studies.[2, 3] As not all of these authors presented their results in this form, it has been necessary to recalculate the coefficient making use of appropriate auxiliary data. In this form these curves represent as nearly as possible the original data, independent of computations involving drift and random speeds. Since their data up to the present have been interpreted only in the light of an attachment process, incipient electron production has appeared as a falling off of the attachment coefficient. It is in the region where α/p and η/p are of comparable magnitude that three of their curves exhibit a sharp decline.

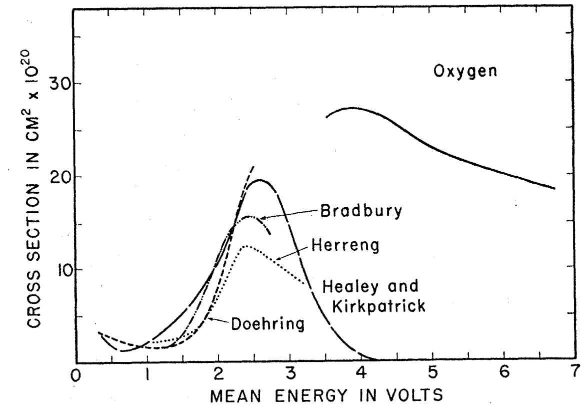

FIG. 10. Mean cross section for attachment in oxygen plotted against mean electron energy. All curves are calculated from those of Fig. 7 using the auxiliary data of reference 29.

Figure 8 presents the attachment coefficient in air and, for comparison, that deduced from Bradbury's paper.[23] It will be noted that the magnitude of the coefficient is considerably less than in oxygen. It is expected that it be less in approximately the ratio of the mole fractions of oxygen in the two gases, in other words, that the peak in air should be about 0.02 attachments per cm per mm. It seems reasonable that such a value would be attained at higher E/p than could be reached by the present apparatus. The positive slope over most of this curve as contrasted with the negative slope observed in oxygen is attributed to the differing energy scales of the two gases. Our data seem to indicate, within the precision of the method, a slight upturn below $E/p=30$. We are hesitant about the validity of this feature, particularly since the curve should in some manner join that of Bradbury. Whereas in oxygen, the coefficients measured in other researches rise to a magnitude comparable with that found in the present work, this is by no means true in air. For this we have as yet no explanation.

In Fig. 9 are given the attachment coefficients for freon-12 and CF_3SF_5 as functions of E/p. Their magnitudes are comparable with that reported for iodine,[25] and considerably larger than that found in chlorine[26] or expected for fluorine. The data in CF_3SF_5, which were taken early in the work show considerable scatter, and the curve is sketched only to indicate a possible behavior for this gas. The large magnitude of η/p in these substances might reflect the possibility for multiple reactions of type B. Here again it is apparent that the large probability for attachment could cause a serious underestimate of the rate of electron multiplication.

It is of some interest to point out that in the range of pressures employed no dependence on this parameter has been detected for any of the gases studied.

2. Dependence of Mean Cross Section on Mean Energy

In oxygen and in air it is possible to make further calculations. Auxiliary data exist from which the variation of mean cross section for negative ion production can be correlated with mean electron energy. The cross section is related to η/p by the equation $\sigma=(\eta/p)\times(v_e/c)(1/n_0)$, where n_0 is the number of molecules per cm^3 at a pressure of one mm of mercury, v_e is the drift speed of the electrons, and c their mean speed of agitation. The mean energy is obtained from diffusion measurements in a manner due originally to Townsend.[27]

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[21] F. H. Sanders, Phys. Rev. **41**, 667 (1932); **44**, 1020 (1933).

[22] B. M. Hochberg and E. J. Sandberg, J. Tech. Phys. (U.R.S.S.) **12**, 65 (1942).

[23] N. Bradbury, Phys. Rev. **44**, 883 (1933).

[24] R. H. Healey and J. W. Reed, *The Behavior of Slow Electrons in Gases* (Amalgamated Wireless, Sydney, 1941), p. 94.

[25] R. H. Healey, Phil. Mag. **26**, 940 (1938).

[26] V. W. Bailey and R. H. Healey, Phil. Mag. **19**, 725 (1935).

Several sets[24,27–30] of data of this kind in oxygen and air have been reported, with considerable discrepancy among them. The discrepancies are relatively unimportant in the calculation of cross sections, as only the ratio of the above speeds enters; hence the magnitudes of σ are probably correct in the two gases. As the energy scales (variation of mean energy with E/p) reported by these authors differ widely, it has been necessary to adopt one for each gas on an almost arbitrary basis. In the case of oxygen the data of Brose[29] have been used. Townsend and Tizard[27] present the most complete data for air, but the recent work of Huxley and Zaazou[30] is probably more reliable. Since the latter authors give no data for $E/p > 25$, an extrapolation has been made.

Results of these computations are given in Figs. 10 and 11, for the cross sections compiled from our results and, for comparison, the work of the other investigators. All curves have been plotted using values of η/p from Figs. 7 and 8 and with auxiliary data as indicated in the previous paragraph. In oxygen the maximum agrees in magnitude with the estimate of Massey, 80×10^{-20} cm^2 for the type B reaction, if one recalls that the present value is an average over the energy distribution. Since this author's estimate of the (unaveraged) cross section for the type C reaction is smaller by a factor of almost 4, additional weight is added to the reasons for adopting B as the principal process. The maxima in oxygen and air again should be nearly in the ratio 5:1, deviation from this value being caused by differing energy distributions. Present data are not inconsistent with this conclusion. The increase of cross section as the mean energy approaches thermal values has been attributed to a reaction of type A.[31–33] The peak found at somewhat higher energy by several workers (see Fig. 10) has been correlated with a level of the oxygen molecule at 1.62 volts.[23,34] Inelastic collisions at this energy, it has been suggested, return electrons to the very low energy region where they are captured by reaction A. Hagstrum[35] and others,[17] however, have shown that reaction B has an appearance potential of 6 volts and a peak probability at 8 volts. The previously mentioned estimate for the height of this peak (80×10^{-20} cm^2) provides sufficiently well for the presently observed maximum to indicate that dissociative attachment is responsible in large part for the observed behavior of the oxygen. Since the excitation function for the 1.62-volt level is presently unknown, the contribution of this "reflection" process cannot be estimated.

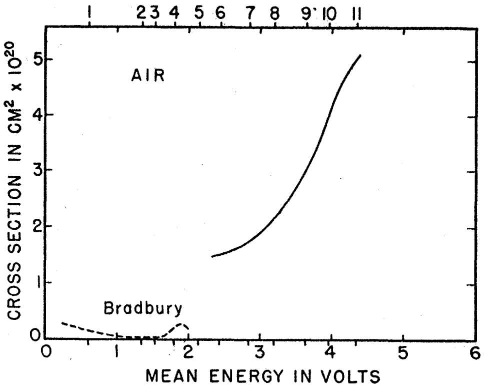

FIG. 11. Mean cross section for attachment in air plotted against mean electron energy. The scale at the bottom refers to the work of Townsend and Tizard. That at the top is due to Huxley and Zaazou, although energies above 6 volts are obtained by extrapolation.

The authors wish to acknowledge helpful comments by interested friends, in particular those of Professor L. B. Loeb of the University of California.

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[27] J. S. Townsend and H. T. Tizard, Proc. Roy. Soc. (London) **A87**, 357 (1912); **A88**, 336 (1913).

[28] J. S. Townsend and V. A. Bailey, Phil. Mag. **42**, 873 (1921).

[29] H. L. Brose, Phil. Mag. **50**, 536 (1925).

[30] L. G. H. Huxley and A. A. Zaazou, Proc. Roy. Soc. (London) **A196**, 402 (1949).

[31] F. Bloch and N. Bradbury, Phys. Rev. **48**, 689 (1935).

[32] M. Biondi, Phys. Rev. **84**, 1072 (1951).

[33] H. S. W. Massey, *Negative Ions* (Cambridge University Press, Cambridge, 1950), second edition, p. 72.

[34] D. R. Bates and H. S. W. Massey, Trans. Roy. Soc. (London) **A239**, 269 (1943).

[35] H. D. Hagstrum, Revs. Modern Phys. **23**, 185 (1951).