Anomalies in Ionization Coefficients and in Uniform Field Breakdown in Argon for Low Values of E/p*

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Prebreakdown ionization currents in argon have been measured in uniform fields for low values of the ratio of field strength to pressure E/p [5 to 12 v (cm mm Hg)$^{-1}$]. Currents obtained with varying electrode separation d at constant E/p and constant p could not be analyzed to yield values of the Townsend coefficients α/p and γ. Currents obtained with varying p at constant E/p and constant d could be analyzed to yield values of α/p and γ, but such currents yielded coefficients which depend on d. The dependence of the values of α/p on d is attributed to the production of highly excited atoms by resonance radiation at some distance from the positions where the electrons lose their energy; these highly excited atoms then produce molecular ions and electrons in collisions with ground-state argon atoms. The secondary mechanism and the dependence of γ on d are associated with resonance radiation. Sparking potential measurements in argon made by varying both p and d for values of pd corresponding to breakdown for the above range of E/p show deviations from Paschen's law.

Disregarding the above anomalies, the values of α/p are smaller than the earlier measurements of Kruithof and Penning by as much as a factor of 15 at $E/p=5$ ($d=4$ cm). At this value of E/p (and of d), the value of $\exp(\alpha d)$ at breakdown is only 1.05, and the value of γ is about 20. At larger values of E/p, the present values of α/p become independent of d and approach theirs. The sparking potentials obtained are significantly larger than those obtained by Kachickas and Fisher. This is shown to be due to the condition of the cathode surface.

INTRODUCTION

IN conjunction with formative time lag breakdown studies in argon, Kachickas and Fisher[1] also measured uniform field breakdown potentials in argon.[2] These breakdown measurements were obtained for products of pressure p and electrode separation d between approximately 200 and 2000 cm mm Hg.[3] This pd range corresponds to a region of electric field strength E divided by p of between approximately 7 and 20 v (cm mm Hg)$^{-1}$ at breakdown.[4] KF combined Kruithof and Penning's[5] measurements of the first Townsend coefficient divided by pressure α/p (which extended down to an E/p of 5) and their own breakdown measurements to obtain a primary multiplication $\exp(\alpha d)$ of only about 2 at breakdown. Assuming the Townsend breakdown condition, this implies an extremely large value (about unity) for the second Townsend coefficient γ (the number of secondary electrons liberated at the cathode in any manner per positive ion incident on the cathode) for the brass cathode used in their study. This value of γ was considered extremely large; in fact, the largest value of γ in argon which had been reported was 0.0376 for a copper cathode.[6] This latter value was obtained by KP from prebreakdown ionization currents at an E/p of 16.55 (the lowest value of E/p for which they reported a value of γ). There was some doubt about KF's conclusion that γ is of the order of unity because their breakdown potential measurements were about 40% lower than the existing breakdown measurements of Penning and Addink[7] and Ehrenkranz.[8] These latter authors had measured breakdown potentials for $pd<300$. Subsequent breakdown measurements by Menes[9] for $pd<500$ are closer to those of Penning and Addink and Ehrenkranz than to those of KF. The present work was undertaken to measure sparking potentials in argon for $100<pd<3000$, and to obtain values of γ (and incidentally also values of α/p) from prebreakdown currents within the range of E/p corresponding to breakdown in this pd range. From these measurements, it was hoped to resolve the conflicting breakdown measurements of previous investigators and to see if the enormous value of γ suggested by KF was indeed correct. There was additional interest in studying the second Townsend coefficient in argon. KF in trying to explain their formative time-lag measurements suggested a delayed photon mechanism (probably diffusion of resonance radiation) for the controlling process in uniform-field breakdown. Subsequently Colli and Facchini[10] observed delayed photon production in cylindrical geometry which they explained as decay of a molecular metastable formed in a collision between two ground-state atoms and an atomic metastable. In addition, Menes[9] studied the growth of current with time in uniform fields at voltages above breakdown and found that his results also required a delayed-photon mechanism. His results for pressures much above 300 could not distinguish between the process outlined by Colli and Facchini and the imprisonment of resonance radiation. For $p<100$, Menes' results definitely ruled out the molecular metastable mechanism. It was hoped that

* This work was supported by the Office of Naval Research and the Army Research Office (Durham).
[1] G. A. Kachickas and L. H. Fisher, Phys. Rev. 91, 775 (1953). (This paper will be referred to as KF.)
[2] Unless otherwise mentioned, all statements in this paper refer to argon.
[3] Unit of d is cm throughout. Unit of p when not otherwise specified is mm of Hg at 0°C.
[4] Units of E/p are volts (cm mm Hg)$^{-1}$ throughout.
[5] A. A. Kruithof and F. M. Penning, Physica 3, 515 (1936). (This paper will be referred to as KP.)
[6] This statement about the value of γ refers to ordinary metallic cathodes such as copper, brass, iron, and nickel, and excludes such cathodes as BaO, etc., for which much larger values of γ have been obtained.
[7] F. M. Penning and C. C. J. Addink, Physica 1, 1007 (1934).
[8] F. Ehrenkranz, Phys. Rev. 55, 219 (1939).
[9] M. Menes, Phys. Rev. 116, 481 (1959).
[10] L. Colli and U. Facchini, Phys. Rev. 88, 987 (1952); L. Colli, Phys. Rev. 95, 892 (1954).

a static study of ionization coefficients would give further information on some of the above points.

The usual equation for the gas current in a uniform dc electric field below breakdown may be written

$$I=I_0 \exp[(\alpha/p)pd]/\{1-\gamma[\exp((\alpha/p)pd)-1]\}, \quad (1)$$

where I_0 is the externally produced photoelectric current at the cathode. In this equation γ is the number of secondary electrons liberated at the cathode in any manner per positive ion incident on the cathode. This equation does not take into account space charge and other effects not proportional to I_0. If α/p and γ are assumed to be functions of E/p only, these coefficients may be evaluated at a particular value of E/p by measurement of prebreakdown currents at various values of pd at this same value of E/p with the use of Eq. (1). In the form in which Eq. (1) is written, it is seen that p and d enter on an equal basis for measurements carried out at constant E/p. In this case, once values of these coefficients are obtained at a given value of E/p, it is possible to predict values of I/I_0 at this value of E/p for any set of values of p and d.

Invariably, α/p is assumed to be a function of E/p only and experimental data in many gases show this to be the case over a wide range of E/p, p, and d. However, Hornbeck[11,12] has suggested the possibility that α/p may be pressure dependent in the rare gases at suitably low values of E/p and p. In addition, Loeb[13] points out the possibility that if electrons are produced in the gas at positions different from the positions where the electrons originally lose their energy, then $\exp(\alpha d)$ loses its conventional meaning. To date, no such anomalies in α/p have been reported. Furthermore, it has been indicated by various authors that γ may not be a function of E/p only.[14–16] Such effects are not taken into account in Eq. (1); if such effects do exist, one might expect difficulty in extracting meaningful coefficients from the data using Eq. (1).

APPARATUS

The discharge chamber used in this work has been described previously.[17] The ultimate pressure attainable in the chamber is about 10^{-6} mm Hg. The gas pressure was measured by means of a mercury manometer between 20 and 760, and with a Dubrovin gauge between 1 and 20. A continuously variable 0–30.1 kv negative dc power supply was used whose short term stability is about 0.001%.[18] A 10-meg resistor was in series with the power supply and a total of 100 meg was in parallel with the chamber. One hundredth of the total voltage across the chamber was measured by a precision differential dc voltmeter. Ionization currents were measured by an electrometer.

EXPERIMENTAL PROCEDURE

In contrast to molecular gases, ionization currents and breakdown potentials for argon were found to change radically with time unless special precautions were taken to stabilize the cathode. After filling the chamber with argon[19] (usually to some pressure between 0.5 and 1 atmosphere), the cathode was irradiated with ultraviolet light and the voltage was raised until the current through the chamber was about 10^{-6} amp. (The current for a particular voltage usually decreased with time, sometimes falling to as low a value as 10^{-10} amp in a few hours.) The voltage was raised from time to time to maintain the current at about 10^{-6} amp until the current became stable to within about a factor of two at some voltage. This process usually took a few days and resulted in prebreakdown currents constant at any voltage to within a few percent over a period of hours providing (1) such currents were limited to less than 5×10^{-9} amp, (2) the gas pressure was not allowed to go below 10^{-3} mm Hg, and (3) sudden changes in voltage were avoided. During the stabilization process the breakdown potential increases with time in a spectacular manner. However, once the cathode is stabilized, the breakdown potential remains constant. Although the properties of the cathode changed slowly with time, the surface did not have to be restabilized for weeks for ionization current measurements carried out within a few hours if conditions (1), (2), and (3) were satisfied. For breakdown, the surface had to be restabilized only if condition (2) was not satisfied. The cathode could also be stabilized to the same degree described above by allowing an intermittent spark discharge to pass between the electrodes for about 50 hr at any pressure between 0.5 and 1 atm. Actually a combination of the two stabilization procedures was used.

In the past, with one exception,[17] Townsend coefficients have been evaluated from prebreakdown currents obtained by varying d at constant p and constant E/p. In the present work, coefficients were evaluated from currents obtained by varying p at constant d and constant E/p. However, some current measurements were also made at constant p and varying d, but such measurements did not lead to the evaluation of any coefficients. To determine the ionization currents as a function of pd at constant E/p and constant d, p was first increased from the minimum to the maximum value

[11] J. A. Hornbeck, Phys. Rev. **84**, 1072 (1951).
[12] Hornbeck's suggestion is described in detail by L. B. Loeb, *Basic Processes of Gaseous Electronics* (University of California Press, Berkeley, California, 1955), pp. 703–708.
[13] See reference 12, p. 702.
[14] R. R. Newton, Phys. Rev. **73**, 570 (1948).
[15] J. P. Molnar, Phys. Rev. **83**, 933 (1951); **83**, 940 (1951).
[16] A. V. Phelps, Phys. Rev. **117**, 619 (1960).
[17] D. J. DeBitetto and L. H. Fisher, Phys. Rev. **104**, 1213 (1956).
[18] This power supply was specially designed and constructed by Beva Laboratories, Trenton, New Jersey.

[19] The argon used in these experiments was Linde commercial tank gas. A mass spectrographic analysis of a sample of gas in contact with the chamber yielded the following analysis by volume: Ar 99.9%, CO_2 0.008%, CO 0.04%, H_2 0.05%, aliphatic hydrocarbons through C_2's 0.004%. We are indebted to Dr. N. B. Hannay and Dr. E. E. Francois of the Bell Telephone Laboratories for this analysis.

used in an experiment in ten to fifteen steps, and then was decreased back to the minimum value in three or four steps. The values of I_0 in these studies were always between 10^{-12} and 10^{-10} amp (usually about 10^{-11} amp).

During the course of the work, it became desirable to test Paschen's law in argon, and therefore breakdown potentials were measured as a function of p and d separately. In these breakdown measurements, after the usual stabilization procedure, p was set at about 700 and the breakdown potential was measured as d was decreased from 4 to 0.5. The breakdown potential was then measured at a somewhat lower pressure as d was increased from 0.5 to 4. Such breakdown measurements were carried out at successively lower pressures with alternately decreasing and increasing values of d until a pressure of about 100 was reached. The entire set of breakdown measurements was then repeated except that p was successively increased from 100 to 700. The breakdown measurements were carried out with ultraviolet illumination of the cathode such that $I_0 \sim 10^{-11}$ amp. With a stabilized surface, the breakdown potentials were reproducible to 0.1%.

PREBREAKDOWN CURRENTS

Prebreakdown currents were measured for $5 \leqslant E/p \leqslant 12$ both by varying p at constant d, and by varying d at constant p. At each value of E/p, such measurements were carried out either at a number of different constant values of d, or at a number of different constant values of p. The prebreakdown currents obtained at constant E/p and constant p with varying d could not be fitted by Eq. (1) with any set of values of I_0, α/p, and γ, and the subsequent discussion of ionization coefficients, unless otherwise noted, refers to prebreakdown currents obtained by varying p at constant d.

For prebreakdown ionization current measurements obtained with a given value of E/p and d, there is an upper limit for p determined by breakdown. This may be called the sparking pressure in analogy to the term sparking distance used in connection with experiments carried out at constant E/p and constant p. For a given value of E/p, as d is increased the maximum permissible pressure decreases and may not allow a large enough pressure variation for accurate determination of α/p and γ. In addition, in order to maintain a reasonably uniform field it was arbitrarily decided never to exceed an electrode separation of 5. These factors determined the largest value of d studied at any E/p. The lower limit for d at any one value of E/p is determined by the fact that the highest pressure possible in the chamber is atmospheric; this may be too far below the sparking pressure to allow accurate calculation of α/p and γ. In addition, d was never allowed to be less than 0.5 cm in order to avoid large percentage errors in the values of d. The above considerations lead to the upper and lower limits of d actually used as a function of E/p as shown in Fig. 1.

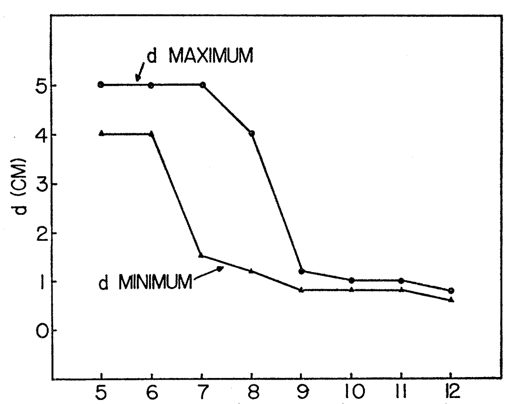

FIG. 1. Upper and lower limits of electrode separation d used in prebreakdown studies at various values of E/p.

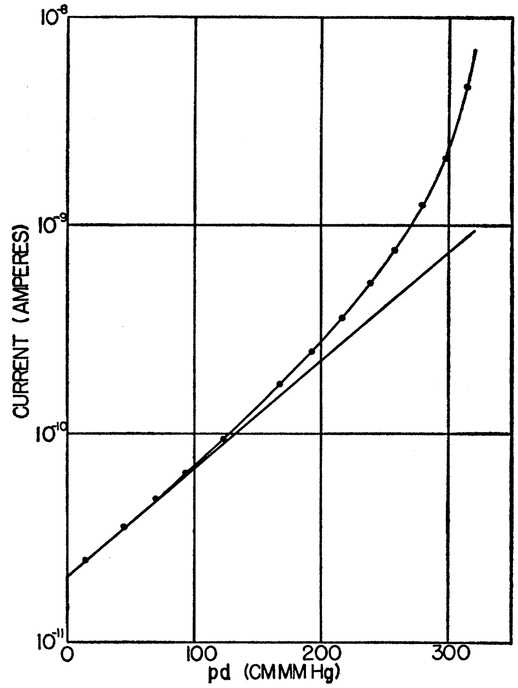

FIG. 2. Points give prebreakdown ionization currents measured at $E/p=12.0$ and $d=0.800$ as a function of pd. Upper curve represents calculated values of currents as described in text. Lower curve represents calculated values of currents with $\gamma=0$ as described in text.

The points in Fig. 2 represent observed prebreakdown ionization currents plotted as a function of pd obtained at $E/p=12.0$ and $d=0.800$, and the points in Fig. 3 were obtained at $E/p=5.00$ and $d=4.00$. Figures 2 and 3 represent the upper and lower values of E/p studied. The E/p range from 5 to 12 corresponds approximately to E/p at breakdown for $400<pd<3000$. In Figs. 2 and 3, the upper curves are currents calculated from Eq. (1) using values of I_0, α/p, and γ obtained from the experimental points in a manner to be described. The straight lines in these figures represent the currents

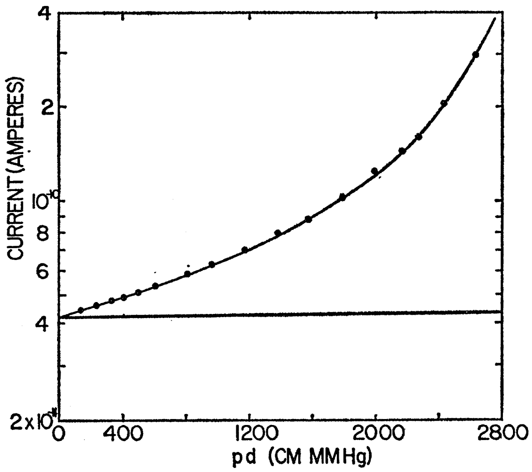

FIG. 3. Points give prebreakdown ionization currents measured at $E/p=5.00$ and $d=4.00$. Upper curve represents calculated values of currents as described in text. The practically horizontal line represents calculated values of currents with $\gamma=0$ as described in text.

which would be calculated with $\gamma=0$ and with the values of I_0 and α/p used in calculating the upper curves. In Fig. 2, the two calculated curves coincide for $pd<75$. In this particular case (where γ turns out to be about 0.02), α/p may be determined to about 2% from the slope of a straight line passing through the experimental points at low enough values of pd. For the data of Fig. 3, analysis gives $\alpha/p\sim10^{-5}$ and $\gamma\sim20$. If a straight line were drawn through the experimental points of Fig. 3 at low pd and α/p evaluated from its slope, the resulting value of α/p would be too large by a factor of 100. This error results because γ is not small compared to unity; for sufficiently small values of pd, Eq. (1) may be written

$$\ln(I/I_0)=(1+\gamma)(\alpha/p)pd. \qquad (2)$$

Thus, the slope of a line drawn through the experimental points will not approach α/p in the limit that pd goes to zero unless $\gamma\ll1$. In the present work, γ cannot in general be neglected in comparison to unity; therefore the following method of successive approximations was used to obtain values of α/p and γ from prebreakdown currents obtained at constant E/p and constant d.

A first approximation of I_0 good to about 10% may be obtained by extrapolation of a plot of $\ln I$ vs pd to $pd=0$ at a given value of E/p. A first approximation to α/p was taken as the slope of this plot for low pd. As shown above, this value of α/p is in general too large by a factor $(1+\gamma)$.[20] Nevertheless, this first approximation to α/p was used to compute values of γ from Eq. (1) for the ten largest experimental currents obtained at a given value of E/p. The initial choice of α/p resulted in calculated values of γ which increase with increasing pd. If a second approximation to α/p was made which was too small, values of γ were obtained which decrease with increasing pd. By varying the choice of α/p, it was found possible to find a few values of α/p differing slightly from each other, each of which gave rise to a set of values of γ which did not vary appreciably with pd. Further small corrections to the above sets were obtained by varying the choice of I_0; this procedure resulted in values of γ which were constant to within 1% for any one set of values of I_0 and α/p. The value of γ chosen to be associated with a particular choice of I_0 and α/p was the average of the ten values of γ calculated at the ten largest values of pd. Each of the above sets of values was used to calculate values of I for all values of pd actually used in an experiment (not only the ten largest). The values of I_0, α/p, and γ chosen as the best set were those which gave a minimum value for the sum of the squares of the percentage differences between the calculated and experimental currents. If the current multiplications for some values of pd are large (as indeed some are in the present work) a conventional least-squares criterion would for all practical purposes ignore the data at small current multiplications. Since all measured currents have approximately the same percentage error, the best fit obtained as described above seems justified.

Measurements carried out at widely separated time intervals gave values of α/p and γ reproducible to within about 10 and 20%, respectively. The values of I_0 at a given value of E/p were varied in some instances from 10^{-12} to 10^{-10} amp without noticeably affecting the calculated values of α/p and γ, thus demonstrating that space charge and other effects not proportional to I_0 can be neglected in the analysis of prebreakdown current data.

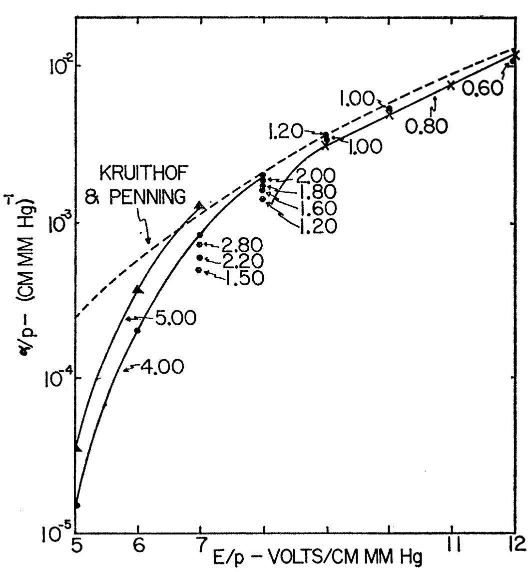

FIG. 4. Points are values of α/p as a function of E/p. Numbers indicate the values of d at which evaluations were made. Solid curves are drawn for $d=5.00$, 4.00, 0.800. Dashed curve shows earlier measurements of α/p of KP.

[20] Unless large enough current multiplication is studied, one may misinterpret a semilogarithmic plot of I vs pd. This may account for the large values of α/p reported by KP for $E/p>9$.

FIRST TOWNSEND COEFFICIENT

Using the above analysis, values of α/p were obtained which increase with d at constant E/p. This variation becomes less pronounced as E/p is increased. At $E/p=5$, the value increases by a factor of 2 when d is increased from 4 to 5; at $E/p=12$, the value does not change appreciably when d is changed from 0.6 to 0.8. The values of α/p obtained as a function of E/p at various values of d are given as points in Fig. 4. The solid curves in the figure are drawn for $d=5.00$, 4.00, and 0.800. The dashed curve in Fig. 4 shows the earlier measurements of KP obtained by varying d at constant p. The present measurements, despite the variation of α/p with d, lie within 20% of their values for $E/p\geqslant 9$. For $E/p<9$, large deviations exist between the two sets of data. The present values are smaller than those of KP by as much as a factor of 15 at $E/p=5$.[20] These results indicate that at a given value of E/p and d the number of electrons produced per unit length traveled in the field direction by each electron varies with the distance from the cathode. Thus a true value of α/p in the sense originally used by Townsend does not exist in argon at these low values of E/p; the values given are to be taken as effective values, namely, those values which when inserted into $\exp(\alpha d)$ will give the correct current multiplication in the gas.

SECOND TOWNSEND COEFFICIENT

The values of γ obtained from the above calculations were found to depend not only on E/p but on d as well. The values of γ obtained increase with decreasing d at constant E/p for the range of d shown in Fig. 1. As already mentioned, a value of γ as large as 20 has been found at $E/p=5$, ($d=4$). With increasing values of E/p, the values of γ obtained decrease sharply, reaching a value essentially independent of d of about 0.02 at $E/p=12$. The values of γ as a function of E/p are given as points in Fig. 5 for various values of d. Curves are drawn for $d=5.00$, 4.00, 1.20, 1.00, and 0.800. There are no previously reported values of γ for argon in this E/p region. KP's value for γ of 0.037 for a copper cathode at $E/p=16.55$ is to be compared with the value of 0.02 at $E/p=12$ obtained in the present work for a nickel cathode.

BREAKDOWN MEASUREMENTS

In view of the fact that α/p and γ were found to depend on d as well as on E/p, it seemed desirable to test Paschen's law over the pd region corresponding to the range of E/p for which ionization currents were measured. Thus breakdown potential measurements were carried out for $100<pd<3000$. In these measurements, as the voltage is increased, a voltage is found at which the current remains unchanged if the ultraviolet light is removed. This threshold voltage is associated with a current of about 10^{-6} amp and was taken to be

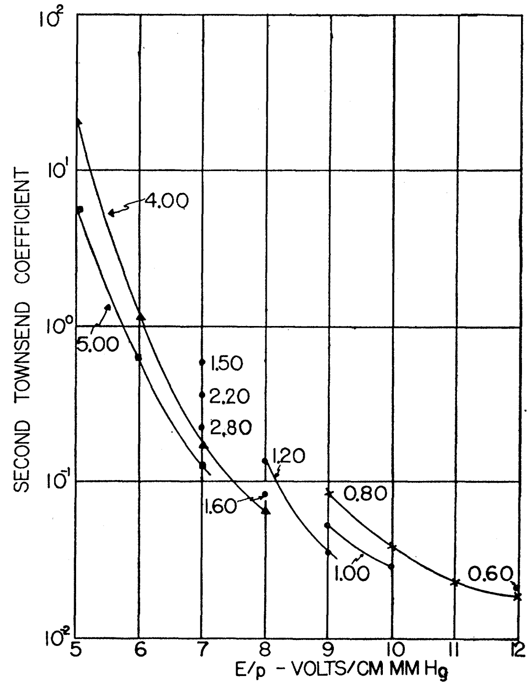

FIG. 5. Points are values of γ obtained at various values of E/p. Numbers indicate the values of d at which evaluations were made. Curves were drawn for values obtained at $d=5.00$, 4.00, 1.20, 1.00, and 0.800.

the breakdown voltage for $50<pd<200$[21,22]; for this pd range the current could be followed up to a few milliamperes without observing a catastrophic breakdown. If the current exceeded 10^{-9} amp, it sometimes displayed positive and sometimes negative characteristics. In any case, all these effects occur within a few volts of the threshold voltage and thus introduce little uncertainty in the measured value of the breakdown potential. For $pd>200$, the same effects were observed, except that a disruptive discharge occurs within a few tenths of a volt above the threshold. In general, in the breakdown studies, currents were limited to about 10^{-6} amp in order to avoid changes in the cathode surface except for single disruptive spark breakdowns. The disruptive breakdowns did not seem to affect the cathode appreciably.

As already mentioned, when a fresh sample of gas is admitted from a base pressure of about 10^{-6} to any

[21] At voltages a few volts below the threshold, the current falls to some fraction of its value if the ultraviolet is removed.

[22] The unchanged current is not a self-sustained current in the sense sometimes used to describe Townsend currents at breakdown. Townsend currents which would be self-sustained because $\gamma[\exp(\alpha d)-1]=1$ would increase linearly with time as long as I_0 is applied. (If there is resistance in the circuit, the voltage at the power supply will have to be raised continuously as long as I_0 is applied in order to keep the voltage across the electrodes at the breakdown value.) Thus the value of a self-sustained Townsend current on the removal of I_0 would remain constant but its value would depend on how long I_0 had been applied before the removal of I_0. Such considerations also neglect the effect of space charge and other effects not proportional to I_0, and to the best of our knowledge such self-sustained currents have never been observed.

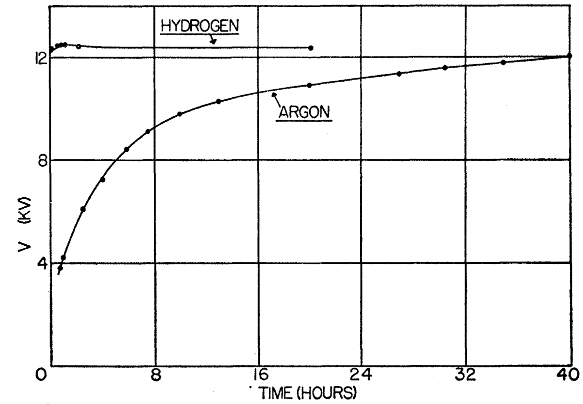

FIG. 6. Sparking potential (V) of argon and hydrogen as a function of time after filling. For argon, $pd=1180$, $d=3.00$; for hydrogen, $pd=558$, $d=2.00$.

given pressure the breakdown potential increases with time in a spectacular manner. The sparking potential increases from some low value to an equilibrium value some four times as large in a period of several days. This time for reaching an equilibrium breakdown value may be reduced somewhat by drawing a current greater than 10^{-6} amp through the chamber. Figure 6 shows a typical curve of breakdown potential in argon vs time after gas filling (with a current of about 10^{-6} amp flowing between measurements). In this particular case, $pd=1180$, $d=3$. One sees that the breakdown potential rose from about 3.8 kv shortly after the gas filling to about 12 kv after a lapse of 40 hr. Some similar breakdown studies at various times after gas filling were also carried out in hydrogen. A typical curve for hydrogen is also shown in Fig. 6 for $pd=558$, $d=2$, where it is seen that the corresponding effect is negligible.

The results of the breakdown measurements with a stabilized cathode are shown as solid curves in Fig. 7. Each curve was obtained at the electrode separation indicated. It is clear that Paschen's law is not obeyed; the breakdown potential at a given pd increases with increasing d. Figure 7 also shows the breakdown measurements of Penning and Addink,[7] Menes,[9] and KF obtained with iron, copper, and brass electrodes, respectively. Aside from the observed deviations from Paschen's law, it is seen that the present values of the breakdown potentials for any given pd are higher than those obtained previously. The sparking potential measurements of KF were made soon after a fresh sample of gas had been admitted to the discharge chamber.[23] This procedure probably accounts in large part for the considerable discrepancies between their breakdown measurements and all others.

DISCUSSION

The fact that I vs pd curves obtained at constant E/p and constant d can be fitted accurately by Eq. (1) with constant values of I_0, α/p, and γ leads one to believe that all ionization occurring in the gas can be described by an effective value of α/p (which varies with d at constant E/p) and that the secondary coefficient γ (despite its variation with d at constant E/p) represents the true number of secondary electrons emitted at the cathode in any manner per positive ion incident on it.

Before discussing the reasons for the anomalous behavior of α/p and γ, some conclusions may be drawn. As explained previously, KF inferred a value of $\exp(\alpha d)$ of only 2 at breakdown. The validity of this conclusion might be questioned since the present values of α/p as well as the present breakdown values are different from the ones they used. However, as already seen, they used values of α/p which are too large and values of the breakdown potential which are too small. These effects, however, compensate each other, and it is now found that the value of primary multiplication $\exp(\alpha d)$ varies from about 1.05 at $E/p=5$, $d=4$ to about 100 at $E/p=12$. One may question whether the small values of α/p observed at low values of E/p are valid measurements of primary ionization or whether α/p is zero. In the latter case, there would be no ionization by collision in the gas (or by any other means), just excitation of atoms to form metastables and/or excited atoms with a consequent release of secondary electrons from the cathode. In this case, γ could not be defined as the number of secondary electrons released at the cathode per positive ion incident on it since there would be no posi-

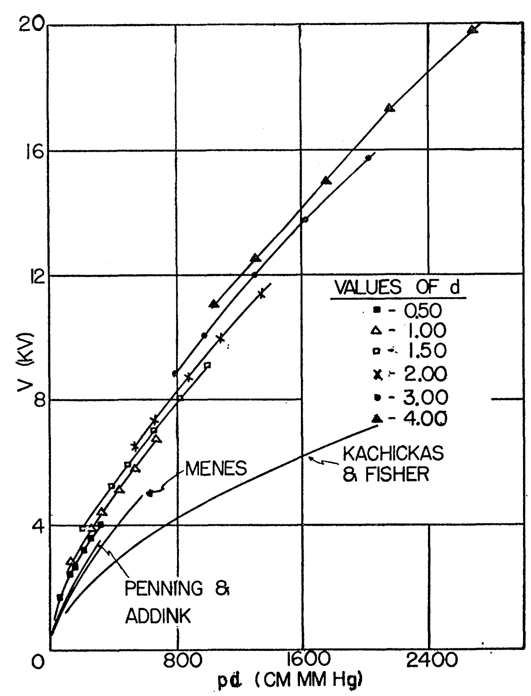

FIG. 7. Sparking potential (V) of argon as a function of pd at various values of d obtained in the present work. Also shown are sparking potential observations of other observers.

[23] G. A. Kachickas, Ph.D. thesis, New York University, 1950 (unpublished).

tive ions formed in the gas. However, despite the small values of α/p at low values of E/p, it is impossible to fit the current data over the entire pd range at a given E/p by a suitable equation ignoring primary ionization. It is thus believed that the values of α/p do represent ionization in the gas. The remarkable increase in sparking potential with time after gas filling means that the value of γ is decreasing radically with time. Since at equilibrium, the value of γ can be as large as 20, the value of γ at the time of a fresh gas filling may be enormous indeed.

The anomalous behavior of the coefficients and the failure of Paschen's law will now be discussed. It is believed that the observed variations of α/p and γ with d at constant E/p in argon and the failure of Paschen's law in argon cannot be ascribed to nonuniformity of the fields. Experiments in hydrogen and nitrogen previously carried out in the same chamber over a pressure range corresponding to that used in the present work and with $d<3.5$ demonstrated that α/p in these gases is a function of E/p only.[17,24] Thus it is not likely that the variation of α/p with d found for argon is due to nonuniformity of the electric fields. To investigate whether the observed deviations from Paschen's law in argon were due to nonuniformity of the electric fields, it was decided to measure breakdown potentials in hydrogen in the chamber as a function of p and d separately. No deviations from Paschen's law were found over a wide range of p and d. It is believed that the above effects are not due to impurities because of their high ionization potentials. In addition, Freely[25] has observed similar effects in spectroscopically pure helium in apparatus using ultra-high vacuum techniques.

As already indicated, there are some effects which if active may cause α/p and/or γ to lose their conventional meanings or dependencies. Several such processes will now be discussed. If in addition to ionization, electrons produce excited atoms which emit resonance radiation, this radiation may diffuse. In this case, excited atoms will appear at appreciable distances from the positions at which the electrons originally lost their energy. It has been established by Hornbeck and Molnar[26] that a highly excited argon atom ($\sim$15 ev) when colliding with a ground-state argon atom can produce a molecular ion and an electron. The creation of such electrons in the body of the gas would cause anomalies in α/p as mentioned by Loeb.[13,27] The above effect may be responsible for the dependence of α/p on d and its independence of p since Holstein[28] has shown that the diffusion of resonance radiation is relatively independent of pressure but

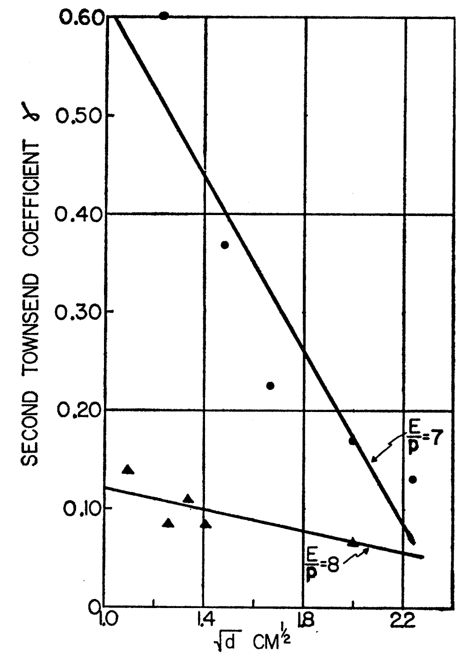

FIG. 8. Values of γ vs $d^{\frac{1}{2}}$ for $E/p=7$ and 8.

depends on d.[29] Since it has been established by Hornbeck and Molnar[26] that metastable argon atoms cannot produce molecular ions, it is felt that metastables cannot be the cause for the anomalous behavior of α/p. The mechanism outlined by Colli and Facchini[10] even if active would produce no ionization in the gas and thus could not account for the observed dependence of α/p on d.

The enormous values of γ indicate that the secondary action is due to photoelectric action at the cathode or to metastable bombardment of the cathode. However, metastable bombardment of the cathode would make γ a function of p and d as well as of E/p.[14] Since in the present experiments, γ was found to be independent of p, γ must be due to photoelectric action at the cathode. Furthermore, Menes'[9] transient observations right above threshold indicate that metastable bombardment of the cathode is not an effective secondary mechanism. The resonant photons involved in the discussion of α/p must be those coming from highly excited levels. However, photons contributing to photoelectric action at the cathode probably involve the low-lying $^3P_1$ and $^1P_1$ resonance levels in considerable measure. A calculation by Phelps[16] (assuming no anomalies in α/p) shows that for high pressure, when most of the photons reaching the cathode have been converted from resonance to non-resonance photons, γ should be independent of p but should vary as $(1+ad^{\frac{1}{2}})^{-1}$ where a is a constant much less than one. In this case γ varies approximately as

[24] Data up to $d=3$ are given in reference 17; data up to $d=3.5$ are given by D. J. DeBitetto, Ph.D. thesis, New York University, 1956 (unpublished).

[25] J. B. Freely, Ph.D. thesis, New York University, 1960 (unpublished).

[26] J. A. Hornbeck and J. P. Molnar, Phys. Rev. **84**, 621 (1951).

[27] Since the positive-ion mobility measurements in argon of J. A. Hornbeck, Phys. Rev. **84**, 615 (1951), were carried out for $E/p>20$, the effects due to dispersal of molecular ions would not have been observed in that experiment.

[28] T. Holstein, Phys. Rev. **72**, 1212 (1947); **83**, 1159 (1951).

[29] However, Holstein's calculations were made for the case where the only possible mode of photon emission is the resonant one; the mechanism outlined above includes the possibility of degradation of some of the resonance radiation energy into fluorescent radiation and into metastable states.

$(1-ad^{\frac{1}{2}})$. If the values of γ observed in the present experiment are due largely to such photons, then it would explain why it is impossible to analyze prebreakdown currents obtained at constant E/p, constant p, and varying d. Figure 8 shows plots of γ vs $d^{\frac{1}{2}}$ for $E/p=7$ and 8 obtained from prebreakdown current data at constant d and varying p. In view of the fact that there are anomalies in α/p, one might not expect more than a rough agreement with Phelps' calculations. As d is increased, the chance for radiation to reach the cathode is reduced, and the chance for molecular ion and electron formation in the gas is accordingly increased. Thus the fact that γ decreases with increasing d is associated with the result that α/p increases with increasing d.

We now consider whether three-body destruction of atomic metastables in the gas and subsequent emission of nonresonant photons as discussed by Colli and Facchini[10] contributes in any sensible measure to γ. From the destruction rate of metastables inferred by Colli,[10] it follows that this effect, if active, should be strongly dependent on p for $p<150$. Since our values of γ were evaluated with values of p ranging from 700 to 5, it is felt that the process discussed by Colli and Facchini is not operating in the present experiments.

Finally, it may be mentioned that despite the anomalous behavior of α/p and γ, the fact that coefficients can be evaluated which are at least independent of p means that currents at a given d can be predicted at any value of p providing that the coefficients were measured at the same value of d. Although the usefulness of the coefficients in predicting currents is thus markedly reduced from the usual situation, the coefficients still retain some utility for predicting currents. Further study of these effects in noble gases at pressures above atmospheric (and hence low E/p) should prove of great interest.