the Ta had a gas film on it. As observed in this study, flashing the Pt target removed most of the active gas films so that the work function of the Pt used was not less than the accepted work functions of clean Pt of value 5.3 volts.[26] In consequence if the value of the work function alone determines γ_i the γ_i for Ta should be greater than that for Pt. Actually the reverse is true as noted. Again Hagstrum[11] observed that for He^+ ions on Mo after the background gas had formed a monolayer on the target γ_i was lowered by 30 percent while ϕ had not changed by more than 0.1 volt.

A guess as to the nature of this action comes from Hagstrum's observation that the energy distribution of electrons from the gas-covered surface had more slow electrons than that from the clean surface. This indicates that the probability of the excited electron occupying a low level in the range of levels available to it is greater for the gas covered surface than for the clean one. Such a condition would obviously also lower γ_i. The process active may be crudely envisioned as follows: with a clean surface neutralization involves direct interaction with only one electron of the Fermi band. With a covered surface it could well involve two for the electrons causing neutralization can come from a local state produced by an adsorbed gas atom. In general since such a local level does not lie in the Fermi band it will be refilled after neutralization by a metallic electron. Such a two-step process could well act to lower the energy available to the excited electron.

Thus gas coatings not only lower γ_i by raising ϕ, but also lower γ_i by reducing the *available* energy for excitation by a more complicated neutralization process. If the *lowering* of ϕ, for instance by H_2 treatment, is small the value of γ_i can still be decreased by H_2 films because of reduction of available escape energy. Likewise, clean Pt could yield a higher γ_i despite its 0.4-volt higher value of ϕ relatively to Ta, as Ta has a gas film at its surface.

That γ_i increases with ion energy is not surprising since kinetic liberation superposes on potential for all surfaces. For gas treated surfaces the observed increase of γ_i with energy is greater than for clean surfaces. This is to be expected for aside from some "cleanup" of the film by high-energy bombardment more of the high-energy ions penetrate the gas film and interact directly with metallic electrons; i.e., the interaction time with the local gas surface states is decreased relative to that with the lattice.

The initial decrease in γ_i with ion energy, observed *only* with nitrogen ions, can be accounted for by the very high energy of association of N atoms to form N_2 molecules. Thus in addition to the neutralization energy of N^+ ions these can react at the surface to yield N_2 at 9.6 ev and this energy may be available for electron liberation. Such a reaction may take place for slowly-moving low-energy ions and may decrease as ion energy increases.

In conclusion the writer wishes to express his appreciation for the support and encouragement given by Professor L. B. Loeb, who suggested this problem and under whose guidance it was carried out.

[26] H. B. Michaelson, J. Appl. Phys. **21**, 536 (1950).

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Liberation of Electrons by Positive-Ion Impact on the Cathode of a Pulsed Townsend Discharge Tube

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The parallel-plate Townsend discharge triggered by a flash of ultraviolet light on the cathode gives a current to the anode which depends strongly on the value of γ, the number of new electrons liberated from the cathode per positive-ion impact. An expression is derived relating γ to the first Townsend coefficient for ionization by electrons α and the anode-cathode separation X, which provides an easy experimental procedure for arriving at γ. Measurements are then given for γ as a function of E/p, the ratio of field strength to pressure, for Ne, A, and Kr on a freshly cleaned Mo cathode. The values of γ are essentially independent of E/p above 175 volts/(cm×mm Hg) with values of 0.20 for Ne^+, 0.083 for A^+, and 0.053 for Kr^+. At lower values of E/p, γ decreases toward zero, but this decline is probably related to the back diffusion of electrons to the cathode and does not represent a decrease in the basic γ process. With A^+ ions and a nickel cathode coated with activated $BaCO_3$, the value of γ also leveled off at higher E/p at a γ value related to the degree of activation of the $BaCO_3$. Significantly, the value of γ for this surface did not tend toward zero at zero E/p. This may be attributed to a different distribution of electron velocities for the ejected electrons from the coated surface than for the pure surface.

INTRODUCTION

THE emission of electrons from cathode surfaces as a result of positive-ion impacts has been studied for many years, first as an essential to the understanding of the mechanism of gas discharges and more recently as a challenging problem in the field of atomic interactions. Despite the number of years that the problem

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has attracted interest, the resolution of experimental difficulties and uncertainties has only become possible in recent times with the advent of many powerful new tools of electronics research. In the present work, pulsed techniques have been employed with the familiar Townsend type of discharge conditions to yield a highly sensitive measurement of γ, the number of electrons escaping per ion impact. The determination is of significance as a disruptive discharge does not occur, as in the more classical methods of determining γ from the breakdown criterion. A further significance of the present results lies in the correlation with the more direct method of Hagstrum[1] and the extension of his results to a lower-energy domain.

APPARATUS

The pulsed Townsend discharge tube developed by Hornbeck[2] and used by him and by the present writer[3] to measure drift velocities of ions in gases is readily

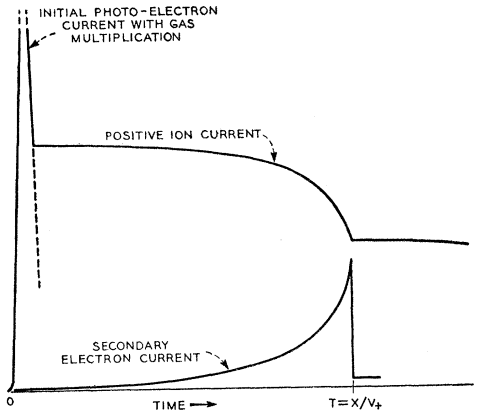

FIG. 1. Schematic resolution of oscilloscope pattern to show positive-ion and electron components of current in the pulsed Townsend discharge tube.

adaptable to the determination of γ, the number of electrons escaping from the cathode per incident ion. As the tube is used, a flash of light of duration approximately 10^{-7} sec liberates photoelectrons from the cathode. The electrons produce positive ions by collision as they drift toward the anode, and the positive ions in turn liberate new electrons as they strike the cathode. A dc potential is maintained across the tube, and a fast oscilloscope is connected to show the current flowing as a function of time following the flash. The current is composed of an electron component and a positive ion component; these are shown schematically in Fig. 1. It is at once clear that the value of γ will strongly influence the pattern appearing on the oscilloscope by its effect on the electron current.

[1] H. D. Hagstrum (private communications). See also Phys. Rev. **89**, 244 (1953).
[2] J. A. Hornbeck, Phys. Rev. **83**, 374 (1951); **84**, 615 (1951).
[3] R. N. Varney, Phys. Rev. **88**, 362 (1952); **89**, 708 (1953).

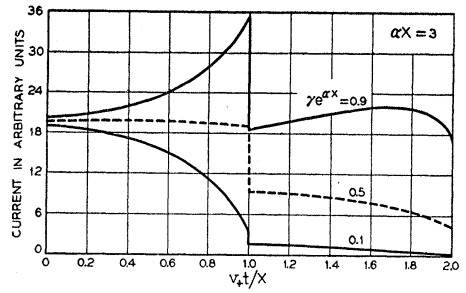

FIG. 2. Graph of Eq. (3) showing three theoretical predictions of oscillograms of the current in a pulsed Townsend discharge tube for a value of $\alpha X=3$ and three values of γ. The calculations applying to times greater than $t=X/v_+$ are not shown in the present paper.

To arrive at a value of γ, a computation has been made of the current to be expected following the flash; it is presented in the appendix. The results of the computation appear below as Eqs. (1)–(3). The current due to electrons i_-, the current due to positive ions i_+, and the total current i which is the sum of i_+ and i_- are given as functions of the time t following the flash, the anode-cathode separation X, and the positive-ion drift velocity v_+. Also appearing in the equations are the electronic charge ϵ, the total number of electrons n_0 emitted by the initial flash, and the first Townsend coefficient α, the number of new electrons liberated by one electron in traveling one cm in the field direction through the gas. The equations are applicable only to the time range, $0\leq t\leq X/v_+$.

$$i_-=\frac{n_0\epsilon v_+}{X}\gamma(e^{\alpha X}-1)e^{\alpha v_+(1+\gamma)t}, \tag{1}$$

$$i_+=\frac{n_0\epsilon v_+}{X}\left[\left(\frac{\gamma}{1+\gamma}e^{\alpha X}-1\right)e^{\alpha v_+(1+\gamma)t}+\frac{e^{\alpha X}}{1+\gamma}\right]. \tag{2}$$

$$i=\frac{n_0\epsilon v_+}{X}\left\{\left[\gamma(e^{\alpha X}-1)+\frac{\gamma}{1+\gamma}e^{\alpha X}-1\right]\times e^{\alpha v_+(1+\gamma)t}+\frac{e^{\alpha X}}{1+\gamma}\right\}. \tag{3}$$

Graphs of Eq. (3) for one value of the parameter αX and for several values of γ are shown in Fig. 2.

The appearance of the horizontal oscilloscope trace in Fig. 2 denotes a constant current, independent of time. Correspondingly, the time-dependent term in Eq. (3) vanishes if the coefficient of that term is zero, or if

$$\gamma(e^{\alpha X}-1)+\frac{\gamma}{1+\gamma}e^{\alpha X}-1=0. \tag{4}$$

Equation (4) may be solved for γ, giving

$$\gamma=[e^{\alpha X}/(e^{\alpha X}-1)]^{\frac{1}{2}}-1. \tag{5}$$

If α and X are known, γ is found at once. The normal range of values of α and of X is suitable to permit evaluation of γ with adequate precision at all values arising in the present paper.

PROCEDURE

Prior to taking readings, the tube was pumped, baked at 400°C, the electrodes glowed by induction heating, and the tube rebaked when necessary. Liquid nitrogen cooling was maintained at all times except during actual runs with krypton gas when liquid oxygen replaced the nitrogen to avoid condensation of the krypton. Residual pressures in the tube following treatment were approximately 4×10^{-9} mm.

With pure molybdenum electrodes, gas of the type to be used in the ensuing experiment was admitted from a high-purity commercial source (tested by mass spectrography and found to contain less than 0.01 percent of foreign matter). A glow discharge was then initiated in the tube and caused sputtering of metal from the cathode surface. As this process progressed, higher and higher currents were forced through the tube, reaching 50 to 100 amperes. The highest currents were of necessity limited to bursts of short duration to avoid overheating. Occasional checks of the discharge characteristics showed the sustaining voltage to be dropping for some time. This voltage ultimately reached a limiting value which agreed with minimum values obtained for the corresponding gases in tube manufacture and believed to be characteristic of pure molybdenum surfaces. Repetition of degassing, activating, and degassing procedures in turn was continued with occasional interruptions for measurements until stability of measurements was attained.

The variables available to the operator for a measurement of γ are the type and pressure of gas in the tube, the anode-cathode separation X, and the dc potential V applied across the tube. The intensity of illumination falling on the cathode is subject to slight variation by insertion or removal of screens. The equipment is set into operation with a pre-set plate separation X, gas pressure p, and no applied voltage, and the voltage is then raised slowly by means of a potentiometer control. In due course, a pattern appears similar to the lowest curve in Fig. 2. With higher voltage, traces resembling the higher curves in Fig. 2 are observed. The values of both α and γ are increasing in this process. Figure 3 shows three superposed oscillograms obtained with applied voltages of 177, 182, and 187 volts, respectively (from bottom to top). The trace which is most nearly horizontal along its first straight section is the one desired, and it is estimated that the required voltage may be selected for this condition within approximately ±1 volt.

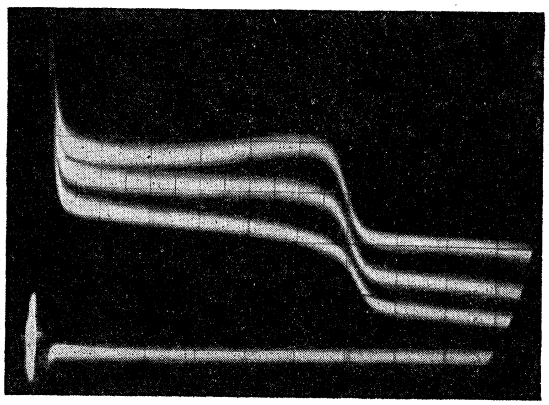

FIG. 3. Three actual oscillograms showing current *vs* time in the Townsend tube for Kr^+ ions in Kr, with a pure Mo cathode. The voltages applied to the tube were, reading upwards, 177, 182, and 187 volts, respectively. Selection of the voltage producing the most nearly horizontal trace may be made much finer than the ±5-volt range illustrated here.

The voltage is then read with a calibrated potentiometer, the plate separation is determined with a measuring microscope, and the pressure is read by means of a calibrated McLeod gauge. The laboratory temperature is recorded. It is then possible to compute E/p_0 as the quantity $V/(273pX/T)$.

In the present work, reference was next made to the work of Kruithof[4] in order to determine a value of α from E/p_0 and p_0 for the rare gases. Kruithof's recommended procedure was followed, wherein αX is replaced by $\alpha(X-x_0)$, thus allowing for the initial distance x_0 in which electrons have not yet acquired ionizing energies. [Kruithof replaces $\alpha(X-x_0)$ by the equivalent $\eta(V-V_0)$.] γ may then be calculated by Eq. (5).

RESULTS

The values of γ for neon, argon, and krypton ions and pure, clean molybdenum cathodes were determined by the procedure described. Additional measurements were made for argon ions in a tube having a cathode coated with $BaCO_3$ and activated partially. The results are plotted in Fig. 4. For the Mo cathode, the value of γ is essentially constant above E/p_0 of 150 to 200, and it takes on value of 0.20 for Ne^+, 0.083 for A^+, and 0.053 for Kr^+. These results may be compared with those of Hagstrum[1] at much higher energies, who has measured γ values on W of 0.24, 0.094, and 0.047 for 10-ev Ne^+, A^+, and Kr^+ ions, respectively. Hagstrum's work shows γ of He^+ (10 ev) on Mo to be about 10 percent less than γ of He^+ (10 ev) on W. One is perhaps justified in concluding that the ion beam experiment would give values for Ne^+, A^+, and Kr^+ on Mo somewhat lower than those quoted above for these ions on W.

At lower values of E/p_0, the values of γ are seen to fall off. While the interpretation of this decline is not assured by the present observations, it is suspected that no change in the basic liberation mechanism is occurring as there is much evidence favoring the independence of γ from the velocity of the incident ions. It is believed,

[4] A. A. Kruithof, Physica **7**, 519 (1940).

however, that at low E and high p, the back reflection of electrons by gas atoms in close proximity to the cathode becomes a mechanism of appreciable significance and may be responsible for the apparent decline in γ.

The observation shown in Fig. 4 for the cathode coated with $BaCO_3$ and activated by a glow discharge in argon is included because of the interest in its shape rather than in the absolute values of γ. The surface is extremely sensitive to virtually any electric current through the tube and may become more strongly activated or deactivated in a short interval of measuring time. The curve shown, however, was traced and retraced several times to establish its validity and the constancy of the surface characteristic throughout the run. Change in the activity of the surface is recognized by a change in the value of γ which has been seen to approach values of 0.5 at the upper limit and to drop below 10^{-3} under less favorable circumstances. The curve shown is an intermediate one.

Surfaces activated to a higher or a lower degree were found to yield curves essentially identical with the one shown but with an altered ordinate scale. All such curves for the $BaCO_3$-coated cathodes differed from those for pure Mo in the shape of the section at low E/p; the former definitely did not approach the origin, whereas the latter essentially did so. The distinction has practical experimental significance because with the pure Mo cathode, the necessary oscilloscope patterns fail to appear below E/p_0 of approximately 40 (volts/cm×mm Hg), whereas they are observable to E/p_0 of 22 for the coated cathode. As E/p_0 is lowered, αX also declines. The product $\gamma e^{\alpha X}$ must be near to 0.5 for the oscillograms desired. If γ and αX both drop, this requirement cannot be met. With the coated cathode, it can be met as γ does not fall toward zero with E/p_0.

The explanation of this behavior of γ at lower values of E/p_0 is believed to be associated with the velocity of ejection of the secondary electrons. If, on the average, the secondary electrons leave at higher speed from the coated cathode than from the pure metal, the back diffusion from the gas is reduced and the apparent value of γ remains higher. Further study of this process is thus indicated.

SOURCES OF ERROR

The uncertainty concerning the origin of the secondary electrons common in determinations of γ is at least partially resolved in the present work. Thus, the emission of secondaries by impact of metastable atoms is completely eliminated from the present observations by the choice of time scales. In the few microseconds during which oscillograms are recorded, metastable atoms drifting at thermal speeds reach the cathode in such trifling numbers as to be insignificant. By the same token, neutral atoms can only be conceivably effective

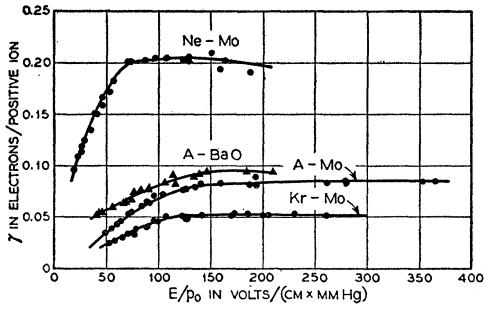

FIG. 4. The values of γ as a function of E/p_0 for Ne^+, A^+ and Kr^+ incident on a clean Mo cathode and for A^+ on a partially activated coated cathode. The degree of cleanness or of activation alters the ordinate scale but not the shape of the curves.

in influencing the observed secondary emission when they are formed from positive ions in the last free path. Radiation originating in the gap from de-excitation and reaching the cathode may influence the apparent secondary emission if it occurs rapidly, that is, in the range of 10^{-8} sec. Molnar[6] indicates that it may account for 7 percent of the total secondary emission. It is a potential factor in the present work, and if Molnar's data are applicable, the values of γ in Fig. 4 must be reduced by the indicated amount.

The rapid aging of clean molybdenum surfaces reported by Molnar in reference 5 did not appear to influence the present results. No decline in γ was observable over a period of several hours during which a curve such as appears in Fig. 4 could be traced and retraced. After 24 hours, with pumping, the values of γ were usually some 10 percent below the previous day's values. Any of a number of seemingly trivial abuses of the tube, however, could precipitate the value of γ to 10^{-3} or even 10^{-4}.

The accuracy of Kruithof's values of α become of significant interest in the determination of γ by the present method. An important question therefore arises whether α cannot be determined directly from these observations. An additional relation connecting αX and γ may be found by comparing the height of the discontinuity at $t=X/v_+$ with the current just before or just after this jump. In theory at least, the simultaneous solution of the new equation with Eq. (5) should yield both αX and γ. In practice, the fractional change in current at the discontinuity as depicted on the oscilloscope screen is sufficiently insensitive to changes in αX or in γ to make it of little practical value for determination of one of these variables. Hornbeck in reference 2 has made some investigation of α by measuring the area under the initial peak of the oscillogram arising from the photoelectron current. Still other procedures for finding α directly in the same experiment are possible, but none has been developed to a suitable precision at the present time.

[6] J. P. Molnar, Phys. Rev. 83, 933 (1951).

CONCLUSIONS

The independence of γ from the kinetic energy of the incident ions has been demonstrated for ions in the range of 4 to 10 times thermal energy. Below approximately 4 times thermal energy, the observed γ declines with decreasing energy but probably because of back diffusion of electrons to the cathode, and not because of any dependence of γ on the ion kinetic energy. For different surfaces, the different nature of the behavior of γ as E/p approaches zero does not contradict this picture provided the velocity distribution of the ejected electrons is also different for different surfaces.

The writer is indebted to Dr. J. A. Hornbeck who designed and constructed the original apparatus and to Dr. B. T. McClure who kindly provided the high-current unit for activating the molybdenum cathode. Dr. McClure and Dr. M. A. Townsend also assisted greatly by providing information on the discharge to molybdenum cathodes which indicated when the cleaning process had reached its limit. Dr. D. J. Rose and Dr. K. G. McKay were most helpful in discussions of the work and criticism of the manuscript. It is also a pleasure to acknowledge the assistance of Mr. F. D. Dolezal who aided extensively with apparatus maintenance, readings, reduction of observations, photography of oscilloscope patterns, and skillful stabilization of the apparatus preceding and during runs.

APPENDIX

The current flowing in the Townsend tube following a very short irradiation of the cathode by ultraviolet light may be analyzed as follows: if the oscilloscope sweep time is adjusted roughly to correspond to the time of transit of positive ions across the tube, electron transit will be so rapid that the regulating feature of the electron current observation will be the rate of liberation of electrons. The current due to positive ions, by contrast, will be determined by the density of ions in the tube at each instant according to the classic Lorentz formula:

$$i_+/A=\rho v_+, \tag{6}$$

where A is the cross-section area of the current.

Initially then, the oscilloscope will show a sharp peak of short duration corresponding to the initial burst of photoelectrons. Whereas the electron burst then vanishes from the picture it has produced a cloud of positive ions, the Townsend avalanche, which is now swept toward the cathode and is responsible for a current component given by

$$i_{+1}=(n_0\epsilon v_+/X)(e^{\alpha X}-e^{\alpha v_+ t}). \tag{7}$$

This equation and all subsequent ones are applicable only to the time interval $0\leq t\leq X/v_+$.

As each ion of Eq. (7) reaches the cathode there is a probability γ that it will release a new electron from the cathode. Such an electron, if it is released, will produce a new avalanche of positive ions yielding a new term in the positive-ion current equation:

$$i_{+2}=(\epsilon v_+/X)\int_0^t \gamma n_+(t')[e^{\alpha X}-e^{\alpha v_+(t-t')}]dt'. \tag{8}$$

The entire integral represents the number of ions formed between 0 and t by the secondary electrons and not yet swept out. The factor $n_+(t)$ represents the number of positive ions per second striking the cathode so that $\gamma n_+(t)$ becomes the number of secondary electrons emitted per second. The electron current from these secondaries is just this amount augmented by the gas multiplication factor (see reference 2) and is thus

$$i_-=n_+(t)\gamma(e^{\alpha X}-1)/\alpha X. \tag{9}$$

Because $n_+(t)$ is as yet undetermined, the positive-ion current which is the sum of (7) and (8) is thus given by an integral equation.

A further relation between i_+ and n_+ is needed. This may be written in the form that the rate of change of i_+ arises from creation of new ions by ionization and sweeping out of old ions by the field. The result is

$$di_+/dt=(\epsilon v_+/X)[n_+(t)\gamma(e^{\alpha X}-1)-n_+(t)]. \tag{10}$$

If the sum of Eqs. (7) and (8) giving i_+ is now differentiated with respect to t under the integral sign and placed on the left side of Eq. (10), the result after clearing is

$$n_+(t)=n_0\alpha v_+e^{\alpha v_+ t}+\gamma\alpha v_+\int_0^t n_+(t')e^{\alpha v_+(t-t')}dt'. \tag{11}$$

Equation (11) is a linear integral equation in n_+ and its solution is

$$n_+(t)=n_0\alpha v_+e^{\alpha v_+(1+\gamma)t}. \tag{12}$$

The values of i_+ and i_- are at once obtained by substitution of Eq. (12) into (7), (8), and (9).

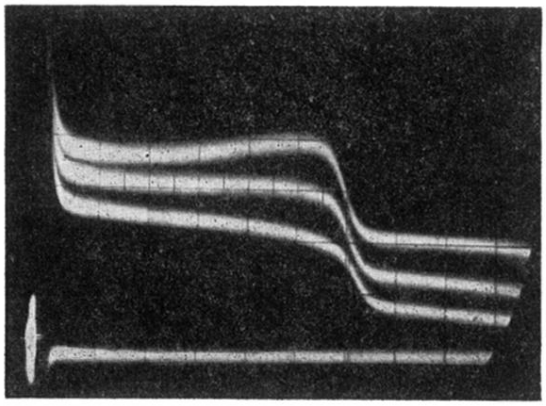

FIG. 3. Three actual oscillograms showing current *vs* time in the Townsend tube for Kr^+ ions in Kr, with a pure Mo cathode. The voltages applied to the tube were, reading upwards, 177, 182, and 187 volts, respectively. Selection of the voltage producing the most nearly horizontal trace may be made much finer than the ±5-volt range illustrated here.