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Role of Molecular Ions, Metastable Molecules, and Resonance Radiation in the Breakdown of Rare Gases

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Theoretical calculations are made of the rates of arrival of atomic and molecular ions, of atomic and molecular metastables, and of nonresonance and resonance radiation at the cathode of parallel plane electrodes during the buildup of current preceding the breakdown of a rare gas. The electron density is assumed to increase exponentially with time and distance. Previous analyses are extended to obtain the particle currents of molecular ions and of metastable atoms and molecules at the cathode. The Holstein-Biberman formulation of the transport equation for the density of atoms in the resonance state is solved numerically to find the fraction of resonance photons arriving at the cathode. The fraction of resonance radiation reaching the cathode varies with the growth constant of the electron current in very nearly the same manner as for delayed photons and varies much less rapidly with electrode spacing and gas density than for the case of diffusing particles. The theory is applied to the calculation of the growth constant as a function of applied voltage for helium at 100 mm Hg pressure and a 1-centimeter gap. The growth of current is found to be controlled by the rates of arrival of molecular metastables, molecular ions, and resonance radiation at the cathode.

I. INTRODUCTION

THE buildup of current following the application of an electric field to a pair of parallel plane electrodes has been the subject of a number of recent experimental and theoretical investigations.[1] If the applied voltage is sufficiently large and the current produced by the external illumination is sufficiently small, the current is observed to increase exponentially with time.[2–4] Recent theory [3,5–7] shows that when one takes into account the discrete nature of the electron avalanches, the expressions for the electron current as a function of time are extremely complicated. However, after a number of transit times of the particle controlling the growth, the time variation of the current can be approximated by a growing exponential, the coefficient of which is the same as that obtained previously using analyses which neglected the discrete nature of the avalanche buildup. Thus, Davidson[5] shows that in the absence of space charge effects, the current buildup is eventually dominated by an exponential whose exponent is the same as that calculated by Steenbeck,[8] by Schade,[1,9] by Bartholomeyczyk,[10] and by von Gugelberg[2] neglecting the discrete nature of the avalanches. These derivations considered only the contributions of positive atomic ions and undelayed photons to the production of electrons at the cathode. Menes[4] has obtained solutions for the case in which

[1] For review of recent work see F. Llewellyn-Jones, *Ionization and Breakdown in Gases* (Methuen and Company, Ltd., London, 1957); and *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 22; P. F. Little, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 21; L. B. Loeb, *Basic Process of Gaseous Electronics* (University of California Press, Berkeley, 1955), Chaps. VIII and IX. We have not made any effort to compare our results with the numerous measurements of formative time lag because of the difficulties encountered in making such a calculation as discussed in the above references and in references 5–7.

[2] H. L. von Gugelberg, Helv. Phys. Acta **20**, 307 (1947). Because of the large values of E/p used in these experiments we do not have basic data as to electron mobilities, etc., required in order to analyze the results.

[3] H. W. Bandel, Phys. Rev. **95**, 1117 (1954).

[4] M. Menes, Phys. Rev. **98**, 561(A) (1955) and Phys. Rev. **116**, 481 (1959).

[5] Dutton, Haydon, Jones, and Davidson, Brit. J. Appl. Phys. **4**, 170 (1953); P. M. Davidson, Phys. Rev. **99**, 1072 (1955); **103**, 1897 (1956).

[6] P. L. Auer, Phys. Rev. **98**, 320 (1955); **101**, 1243 (1956); **111**, 671 (1958).

[7] P. M. Davidson, Proc. Roy. Soc. (London) **A249**, 237 (1959).

[8] M. Steenbeck, Wiss. Veröffentl. Siemens-Konzern **9**, 42 (1930).

[9] R. Schade, Z. Physik **104**, 487 (1937).

[10] W. Bartholomecyzyk, Z. Physik **116**, 235 (1940).

secondary electrons result from delayed photons such as observed by Colli[11] in argon. Very recently, Davidson[7] has obtained solutions for the current growth when the electrons are produced at the cathode by an excited species which arrives at the cathode by diffusion. Diffusion theory is expected to be valid for metastable atoms and molecules but not for resonance radiation.[12,13]

In this paper we shall obtain expressions for use in calculating the contributions of resonance and collision induced photons, molecular ions, and metastable molecules to the electron current produced at the cathode and calculate the contributions of each of the secondary processes to the growth of current in rare gases. Resonance photons are those photons which are emitted in radiative transitions to the ground state. They are readily absorbed by atoms in the ground state and, therefore, they experience considerable difficulty in reaching the cathode from the region of greatest production near the anode. Collision induced photons are those nonresonance photons produced as a result of collisions between metastable atoms and ground-state atoms. In Sec. II we shall obtain the equations governing the density of electrons, ions, and metastable atoms and molecules. These can be solved immediately for the rate of arrival of ions, metastable atoms and molecules, and nonresonance photons at the cathode. In Sec. III the Holstein-Biberman theory[13,14] of imprisonment of resonance radiation is used to find the spatial distribution of resonance atoms and the rate of arrival of resonance photons at the cathode. Finally, the theoretical expressions are used to predict the current growth in helium.

II. GENERAL THEORY

The processes to be considered in the following analysis are:

1. Ionization and excitation of the rare gas atoms by electrons under the action of a uniform electric field between infinite parallel plane electrodes.[15] Electrons liberated from the cathode are assumed to reach their equilibrium velocity distribution in a distance small compared to the electrode separation and to move through the gas with a constant drift velocity. As electrons emitted from the cathode approach their equilibrium distribution, an appreciable fraction of them are scattered back to the cathode.[1,16] For convenience, this "back diffusion" is taken into account by a reduction in the yield of electrons resulting from the various processes discussed below. Some of the excited atoms are assumed to form molecular ions in collisions with ground-state atoms.[17]

2. The atomic and molecular positive ions are assumed to move with a constant drift velocity toward the cathode.[18] It is necessary to take into account the conversion of atomic ions into molecular ions in three-body collisions with two ground-state atoms.[19] Because of the large applied voltages and relatively low average energies of the ions, diffusion of the ions is negligible.[20] When the ions reach the cathode some of them will cause the emission of electrons from the cathode.[1,15] We shall designate the net number of electrons entering the gap per atomic and molecular ion arriving at the cathode by the coefficients γ_1 and γ_2, respectively.

3. The metastable atoms and molecules produced in the region between the electrodes are assumed to be removed from the discharge region by diffusion to the electrodes and by collisions with atoms in the ground state.[21–23] The metastable atoms and molecules can liberate electrons at the cathode[24] when they reach the cathode by diffusion. In addition, the collision of a metastable with a ground-state atom may produce a nonresonance photon which can release an electron from the cathode, e.g., the helium singlet metastable.[21] Un-

[11] L. Colli, Phys. Rev. **95**, 892 (1954).
[12] C. Kenty, Phys. Rev. **42**, 823 (1932); A. V. Phelps and A. O. McCoubrey, Bull. Am. Phys. Soc. **3**, 83 (1958).
[13] T. Holstein, Phys. Rev. **72**, 1212 (1947); **83**, 1159 (1951).
[14] L. M. Biberman, J. Exptl. Theoret. Phys. U.S.S.R. **17**, 416 (1947); **19**, 584 (1949); and L. M. Biberman and I. M. Gurevich, J. Exptl. Theoret. Phys. U.S.S.R. **20**, 108 (1950).
[15] For a review of theory and experimental data on these processes see H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, 1952).
[16] J. K. Theobald, J. Appl. Phys. **24**, 123 (1953).
[17] J. A. Hornbeck, Phys. Rev. **84**, 1072(A) (1951). In this reference α_1/α_2 is estimated to be 0.2 at $E/p=12.7$ volt/cm-mm Hg for helium densities such that $N\gg 1/\tau\sigma v=10^{17}$ atom/cc. J. A. Hornbeck and J. P. Molnar, Phys. Rev. **84**, 621 (1951), give the electron energy dependence of the probability of molecular ion formation. Contrary to their conclusions we believe that the rapid decrease in their data at electron energies above 30 ev shows that the helium molecular ions are formed from excited atoms in the n^3S states (see references 15 and 36 for the shapes of the n^3S excitation curves). If this hypothesis is correct then: (a) The time constant characteristic of this process is equal to or less than that of the radiative lifetime of the n^3S states ($\sim 10^{-8}$ second) and one can neglect the effect of this time delay on the current buildup for $\lambda < 10^7$ second^{-1}. (b) Using the energy dependence of n^3S cross sections and electron energy distribution functions from reference 36, the dependence of α_2/p on E/p is found to be intermediate between that for α_R/p and α_S/p. (c) The magnitude of the α_2/p curve is obtained by fitting a curve of the proper E/p dependence to Hornbeck's datum point at $E/p=12.7$ volt/cm-mm Hg.
[18] For a review of recent theory and experimental data on ion mobilities see A. Dalgarno, Phil. Trans. Roy. Soc. (London) **250**, 426 (1958). Useful empirical expressions for the mobilities of rare gas ions in their parent gas are given by L. S. Frost, Phys. Rev. **105**, 354 (1957). The helium molecular ion drift velocities are from M. A. Biondi and L. M. Chanin, Phys. Rev. **94**, 910 (1954).
[19] A. V. Phelps, Phys. Rev. **86**, 102 (1952).
[20] The mean square distance an electron or ion diffuses in a time, t, is $2Dt$, where D is the diffusion coefficient. To a good approximation the diffusion relative to the point of maximum density is unchanged by the application of a field. Since $t=d/\mu E=d^2/\mu V$, where μ is the ion mobility, the mean square fraction of the electrode distance which an electron or ion diffuses while crossing the tube is approximately $2(D/\mu)/V$. Since experiments show that $D/\mu \ll V$ at breakdown the diffusion of the electrons and ions can be neglected.
[21] For the measurements of the properties of helium metastable atoms and molecules see A. V. Phelps, Phys. Rev. **99**, 1307 (1955).
[22] For studies of neon metastables and resonance radiation see J. R. Dixon and F. A. Grant, Phys. Rev. **107**, 118 (1957); and A. V. Phelps, Phys. Rev. **114**, 1011 (1959).
[23] For argon metastables see A. H. Futch and F. A. Grant, Phys. Rev. **104**, 356 (1956).
[24] R. W. Engstrom and W. S. Huxford, Phys. Rev. **58**, 67 (1940). J. P. Molnar, Phys. Rev. **83**, 933 and 940 (1951).

TABLE I. List of symbols used in theory.

e, 1, 2, a, m, p, r	Subscript designating electrons, atomic ions, molecular ions, metastable atoms, metastable molecules, nonresonance photons, and resonance atoms or photons.
A_I	Imprisonment constant for transport of resonance radiation.
A_r, A_{rm}, A_m	Radiative transition probabilities for the resonance transition, a nonresonance transition, and for a molecular metastable.
B_y	Two-body collisional frequency for species y.
C_{yz}	Three-body collision frequency for conversion of species y into species z.
d	Distance between cathode and anode.
D_y	Diffusion coefficient at unit gas density for species y.
f_{yz}	Number of species z arriving at cathode per electron leaving. The meaning of multiple subscripts is the same as for Γ_{yz}.
$G=A_{rm}+B_r$	Sum of nonresonance transition probability and two-body destruction coefficient for resonance state.
$K(\|x'-x\|)$	Transmission function for resonance radiation.
$n_y(x,t)$	Density of electrons, ions, excited atoms or photons as indicated by subscript y.
n_0	Electron density at the cathode.
N	Density of ground-state atoms, i.e., gas density.
t	Time following the application of voltage to the gap.
v_y	Drift velocity for species y.
x	Distance from cathode toward anode.
α	$\alpha_1+\alpha_2-\lambda/r_-$.
$\alpha_y=\nu_y/v_e$	Number of species y produced during one centimeter drift of electron in field direction.
β	$\lambda+C_{12}$.
γ_z	Yield of electrons at the cathode due to the arrival of species z.
Γ_{yz}	Current density of species z at the cathode. The first subscript gives the state in which the excitation is considered to originate. A third subscript between the y and z denotes an intermediate state.
λ	Current growth constant.
λ_0	Wavelength of resonance radiation.
μ_y	Diffusion parameter for species y.
ν_y	Frequency of excitation of species y at unit gas density.

fortunately, there is a lack of quantitative data available regarding many metastable states of interest. For example, Colli has measured the lifetime of the argon molecular metastable[11] but essentially nothing is known about the rate at which argon atomic metastables are converted into atoms in the resonance state or are destroyed by collision induced radiation.[23] In the case of neon[22] the behavior of the atomic metastables is known but nothing quantitative is known about the existence or properties of metastable molecules. Helium metastable atoms and molecules have been studied more thoroughly.[21]

4. The density of atoms in the resonance state and the rate of arrival of resonance photons at the cathode are assumed to be given by the Holstein-Biberman theory for the imprisonment of resonance radiation.[13,14] The gas densities in the experiments performed with pure gases are usually high enough so that transmission of the resonance radiation is governed by the pressure broadened spectral line. In particular, the collisions effective in determining the broadening are assumed to be of the dipole-dipole type.[13,25] In this case the only properties of the resonance state which we need to know are its natural lifetime[13,26] and the frequencies or rates of collision processes which produce or destroy the resonance atoms. The yield of electrons per photon[27] arriving at the cathode will be designated by γ_p.

The differential equations describing the processes discussed above and governing the densities of electrons, positive atomic ions, positive molecular ions, atomic metastables, molecular metastables, and resonance atoms can be written as follows[1,13,22]:

$$\frac{\partial n_e}{\partial t}=(\nu_1+\nu_2)n_e-v_e\frac{\partial n_e}{\partial x}, \tag{1}$$

$$\frac{\partial n_1}{\partial t}=\nu_1 n_e+v_1\frac{\partial n_1}{\partial x}-C_{12}n_1, \tag{2}$$

$$\frac{\partial n_2}{\partial t}=\nu_2 n_e+v_2\frac{\partial n_2}{\partial x}+C_{12}n_1, \tag{3}$$

$$\frac{\partial n_a}{\partial t}=\nu_a n_e+\frac{D_a}{N}\frac{\partial^2 n_a}{\partial x^2}-B_a n_a-C_{am}n_a, \tag{4}$$

$$\frac{\partial n_m}{\partial t}=C_{am}n_a-B_m n_m-A_m n_m+\frac{D_m}{N}\frac{\partial^2 n_m}{\partial x^2}, \tag{5}$$

$$\frac{\partial n_r}{\partial t}=\nu_r n_e-Gn_r-A_r n_r+A_r \times\int_0^d n_r(x',t)K(|x-x'|)dx'. \tag{6}$$

The symbols used in the equations of this section are defined in Table I. $K(|x-x'|)dx'$ is the probability[13] that radiation emitted at x will be absorbed in a plane of thickness dx' at x'. Note that we have neglected the coupling of the metastable and resonance atom equations resulting from the collisional conversion from atoms in metastable states into atoms in resonance states or vice versa. This possibility will be considered in Sec. III. We also assumed that the photons produced

[25] For a demonstration of the validity of these assumptions in neon see reference 22.

[26] A. G. C. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (The Macmillan Company, New York, 1934), Chap. III.

[27] G. L. Weissler, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 21, pp. 342–370.

in transitions among excited states do not have enough energy to produce a significant photoelectric current at the cathode.[26]

The boundary conditions at the cathode ($x=0$) and anode ($x=d$) are:

$$\Gamma_e(0,t)=v_e n_e(0,t)=\gamma_1\Gamma_1+\gamma_2\Gamma_2+\gamma_a\Gamma_a+\gamma_m\Gamma_m+\gamma_p\Gamma_{ap}+\gamma_p\Gamma_{mp}+\gamma_p\Gamma_r; \quad (7)$$

$\Gamma_1(d,t)=0$; $\Gamma_2(d,t)=0$; $n_a=n_m=0$ for $x=0$ and $x=d$; and $n_r=0$ for $x<0$ and $x>d$, i.e., outside the gap. Here,

$$\Gamma_1=v_1 n_1(x,t), \quad \Gamma_2=v_2 n_2(x,t),$$

$$\Gamma_{a,m}=\frac{D_{a,m}}{N}\frac{\partial n_{a,m}(x,t)}{\partial x}\bigg|_{x=0}, \quad (8)$$

$$\Gamma_{ap}=\frac{B_a}{2}\int_0^d n_a(x)dx, \quad \Gamma_{mp}=\frac{A_m}{2}\int_0^d n_m(x)dx,$$

and

$$\Gamma_r=A_r\int_0^d n_r(x,t)dx\int_{-\infty}^0 K(|x'-x|)dx' =A_r\int_0^d n_r(x,t)dx\int_x^\infty K(y)dy. \quad (9)$$

Note that the equations for Γ_{ap} and Γ_{mp} include the fraction (one-half) of nonresonance photons produced in the gap which reach the cathode. We have assumed that there is negligible reflection of the photons[28] and the metastable atoms and molecules[21-23] at the electrodes. The integral of $K(|x'-x|)$ in Eq. (9) gives the probability that the resonance photons emitted at x will be absorbed at a point to the left of $x=0$ in the absence of the cathode or the probability the resonance photons will travel as far as the cathode before absorption. We have neglected the current due to irradiation of the cathode by an external source.[29]

If we assume that the electron current at the cathode increases exponentially with time, then the solutions to Eqs. (1) and (2) are:

$$n_e(x,t)=n_0 e^{\lambda t}\exp(\alpha_1+\alpha_2-\lambda/v_e)x, \quad (10)$$

and

$$n_1(x,t)=\frac{\nu_1 n_0[\exp(\alpha-\beta/v_1)d-\exp(\alpha-\beta/v_1)x]e^{\lambda t}e^{\beta x/v_1}}{v_1(\alpha-\beta/v_1)}. \quad (11)$$

It is convenient to consider the ratio of the atomic ion current arriving at the cathode to the electron current leaving the cathode, i.e.,

$$f_1=\frac{\Gamma_1}{\Gamma_e}=\frac{\alpha_1[\exp(\alpha-\beta/v_1)d-1]}{(\alpha-\beta/v_1)}. \quad (12)$$

If the atomic ions are the only means of liberating electrons from the cathode, and if the conversion of atomic ions into molecular ions is negligible ($C_{12}\ll\alpha v_1$), we obtain the same result as previous investigators[1] by setting $\gamma_1 f_1=1$ and solving for λ. As shown by Davidson[5] and others,[3,6] the simple exponential solution obtained in this manner is valid only after a sufficient number of ion transit times so that the pulsating behavior of the current has disappeared.

The density of molecular ions in the gap is found by inserting Eqs. (10) and (11) into Eq. (3) to obtain the results that

$$n_2(x)=\left(\nu_2-\frac{C_{12}\nu_1}{v_1(\alpha-\beta/v_1)}\right)\frac{n_0 e^{\lambda x/v_2}}{v_2(\alpha-\lambda/v_2)}[\exp(\alpha-\lambda/v_2)d-\exp(\alpha-\lambda/v_2)x] +\frac{C_{12}\nu_1 n_0 e^{\lambda x/v_2}\exp(\alpha-\beta/v_1)d[\exp(\beta/v_1-\lambda/v_2)d-\exp(\beta/v_1-\lambda/v_2)x]}{v_1 v_2(\alpha-\beta/v_1)(\beta/v_1-\lambda/v_2)},$$

and

$$f_2=\frac{\alpha_2[\exp(\alpha-\lambda/v_2)d-1]}{\alpha-\lambda/v_2}+\frac{C_{12}\alpha_1}{v_1(\alpha-\beta/v_1)}\left(\frac{\exp(\alpha-\lambda/v_2)d-\exp(\alpha-\beta/v_1)d}{\beta/v_1-\lambda/v_2}-\frac{\exp(\alpha-\lambda/v_2)d-1}{\alpha-\lambda/v_2}\right). \quad (13)$$

The first term on the right-hand side of Eq. (13) gives the number of ions arriving per electron leaving due to the ions which were initially formed as molecular ions. The second term gives the contribution of ions which were formed as atomic ions and were converted to molecular ions while drifting toward the cathode.

If the metastable atoms make a significant contribution to a cathode current which rises exponentially with time over a sufficient range of current, then the metastable density must also be increasing exponentially with the same growth constant. In this case the equation governing the metastable density becomes:

$$\frac{D_a}{N}\frac{d^2 n_a(x)}{dx^2}+(B_a+C_{am}+\lambda)n_a(x)=\nu_a n_0 e^{\alpha x}. \quad (14)$$

A solution of this equation which satisfies the boundary

[28] The reflection coefficient for photons of 1000A or less is found to be about 10% or less. G. E. Sabine, Phys. Rev. **55**, 1064 (1939).

[29] Inclusion of the electron current produced by external illumination may produce important changes in the magnitude of the computed current especially at early times, but will not affect the growth constant calculated in this paper. See reference 1.

conditions in Eq. (7) is

$$n_a(x)=\frac{2\nu_a n_0}{\pi}\sum_{j=1}^{\infty}\frac{[1-(-1)^j e^{\alpha d}]\sin(j\pi x/d)}{j[(j^2\pi^2 D_a/Nd^2)+B_a+C_{am}+\lambda][(\alpha^2d^2/j^2\pi^2)+1]}.$$

Substitution of this result into Eq. (5) and writing $n_m(x)$ as a summation gives

$$n_m(x)=\frac{2\nu_a n_0}{\pi}\sum_{j=1}^{\infty}\frac{[1-(-1)^j e^{\alpha d}]\sin(j\pi x/d)}{j[(j^2\pi^2 D_a/Nd^2)+B_a+C_{am}+\lambda][(\alpha^2d^2/j^2\pi^2)+1][(j^2\pi^2 D_m/Nd^2)+C_{am}+A_m+\lambda]}.$$

The current density of metastable atoms reaching the cathode by diffusion is

$$\Gamma_a=\frac{D_a}{N}\frac{dn_a}{dx}\bigg|_{x=0}=2\nu_a d n_0\sum_{j=1}^{\infty}\frac{j^2\pi^2[1-(-1)^j e^{\alpha d}]}{(j^2\pi^2+\mu_a^2)(j^2\pi^2+\alpha^2d^2)}$$

$$=\frac{\nu_a d n_0\mu_a}{(\alpha^2d^2-\mu_a^2)}\left(\frac{e^{\alpha d}-\cosh\mu_a}{\sinh\mu_a}-\frac{\alpha d}{\mu_a}\right),$$

where

$$\mu_a^2=(B_a+C_{am}+\lambda)Nd^2/D_a,$$
$$\mu_m^2=(B_m+A_m+\lambda)Nd^2/D_m,$$

and the summations were made using expansions for coth and cosech.[30] The number of metastable atoms arriving at the cathode per electron leaving is therefore given by

$$f_a=\frac{\alpha_a d\mu_a}{(\alpha^2d^2-\mu_a^2)}\left(\frac{e^{\alpha d}-\cosh\mu_a}{\sinh\mu_a}-\frac{\alpha d}{\mu_a}\right). \quad (15)$$

If $\lambda=0$ this result is the same as that obtained by Davidson.[7,31] If $\mu_a=0$, then $f_a=(\alpha_a/\alpha^2 d)(e^{\alpha d}-1-\alpha d)$, as found by Newton.[32] Note that for $\mu_a=0$ and $\alpha d=0$, $f_a=\alpha_a d/2$, as expected. Also, if $(\mu_a-\alpha d)\geq 6$ and $\mu_a\geq 6$, then $f_a=\alpha_a d/(\mu_a-\alpha d)$ to better than one percent and $f_a/\alpha_a d\leq 0.17$.

Similarly, the number of metastable molecules arriving at the cathode per electron leaving is

$$f_m=\frac{\alpha_a d C_{am}Nd^2}{D_a}\left(\frac{\alpha d}{(\mu_a^2-\alpha^2d^2)(\mu_m^2-\alpha^2d^2)}\right.$$
$$+\frac{\mu_a(e^{\alpha d}\operatorname{cosech}\mu_a-\coth\mu_a)}{(\alpha^2d^2-\mu_a^2)(\mu_m^2-\mu_a^2)}$$
$$\left.+\frac{\mu_m(e^{\alpha d}\operatorname{cosech}\mu_m-\coth\mu_m)}{(\alpha^2d^2-\mu_m^2)(\mu_a^2-\mu_m^2)}\right). \quad (16)$$

If the metastable atoms or molecules radiate spontaneously[11] or are caused to radiate by collisions,[21] there will be a current of photons arriving at the cathode which is proportional to the corresponding transition probability or collision frequency. Thus, the current of nonresonance photons arriving at the cathode due to collision induced radiation from the atomic metastables is given by the relation

$$\Gamma_{ap}=\frac{B_a}{2}\int_0^x n_a dx=\frac{\nu_a n_0 B_a Nd^3(e^{\alpha d}+1)}{D_a}$$
$$\times\sum_{j=1}^{\infty}\frac{[1+(-1)^j]}{(j^2\pi^2+\mu_a^2)(j^2\pi^2+\alpha^2d^2)},$$

so that

$$f_{ap}=\frac{\alpha_a d B_a Nd^2}{2D_a(\mu_a^2-\alpha^2d^2)}$$
$$\times\left(\frac{e^{\alpha d}-1}{\alpha d}-\frac{(e^{\mu_a}-1)(e^{\alpha d}+1)}{\mu_a(e^{\mu_a}+1)}\right). \quad (17)$$

Similarly, the number of photons arriving at the cathode due to the spontaneous radiation and collision induced radiation from metastable molecules per electron leaving the cathode is

$$f_{amp}=\frac{\alpha_a d C_{am}(A_m+B_m)(e^{\alpha d}+1)N^2d^4}{2D_aD_m}$$
$$\times\left(\frac{e^{\alpha d}-1}{\alpha d(\mu_a^2-\alpha^2d^2)(\mu_m^2-\alpha^2d^2)(e^{\alpha d}+1)}\right.$$
$$+\frac{(\coth\mu_a-\operatorname{cosech}\mu_a)}{\mu_a(\alpha^2d^2-\mu_a^2)(\mu_m^2-\mu_a^2)}$$
$$\left.+\frac{(\coth\mu_m-\operatorname{cosech}\mu_m)}{\mu_m(\alpha^2d^2-\mu_m^2)(\mu_a^2-\mu_m^2)}\right). \quad (18)$$

At sufficiently high gas densities or sufficiently large λ $\mu_a^2\gg 1$ and $\mu_a^2\gg\alpha^2d^2$ so that

$$f_{ap}=\frac{\alpha_a B_a(e^{\alpha d}-1)}{2\alpha(B_a+C_{am}+\lambda)}. \quad (19)$$

Similarly, when $\mu_a^2\gg 1$, $\mu_a^2\gg\alpha^2d^2$, $\mu_m^2\gg 1$, and $\mu_m^2\gg\alpha^2d^2$, then

$$f_{amp}=\frac{E(A_m+B_m)}{2(B_a+C_{am}+\lambda)(A_m+B_m+\lambda)}\frac{\alpha_a(e^{\alpha d}-1)}{\alpha}. \quad (20)$$

[30] E. T. Whitaker and G. N. Watson, *A Course of Modern Analysis* (Cambridge University Press, New York, 1944), p. 136.

[31] This result is to be compared with Davidson's solution for the steady state current under conditions of complete absorption of the metastable atoms at the electrodes. In general, the steady-state current is found from our solution by setting $\lambda=0$ and adding the current produced by external illumination, Γ_0, to the right-hand side of Eq. (7). The result is that $\Gamma_e/\Gamma_0=(1-\sum_n\gamma_n f_n)^{-1}$.

[32] R. R. Newton, Phys. Rev. **73**, 570 (1948).

III. CONTRIBUTION OF IMPRISONED RESONANCE RADIATION

The integro-differential equation governing the density of atoms in a resonance state, Eq. (5), becomes an integral equation when we substitute Eq. (10) for the electron density and assume that the resonance atom density is increasing exponentially with the growth constant λ. Thus we obtain the relations

$$\nu_r n_0 e^{\alpha x} = (A_r+\lambda+G)n_r(x) - A_r\int_0^d n_r(x')K(|x-x'|)dx', \quad (21)$$

and

$$f_r=\frac{\Gamma_r}{\Gamma_e}=\frac{A_r\alpha_r}{\nu_r n_0}\int_0^d n_r(x)dx\int_x^\infty K(|y|)dy,$$

where $K(|x-x'|)$ is to be determined from the transmission properties of the gas for resonance radiation. Holstein[13] has shown that if the probability of radiation traversing a distance, ρ, without absorption is given by $T(\rho)=a_m/\rho^m$ then $K(|\rho|)=[ma_m/2(m+1)](1/|\rho|^{m+1})$. Furthermore, he showed that at high enough gas densities the transmission of the resonance radiation is controlled by the collision broadened portion of the spectral line and that when the dipole-dipole interaction dominates, $m=\frac{1}{2}$ and $a_m=(\lambda_0/3\pi^2)^{\frac{1}{2}}$, where λ_0 is the wavelength of the resonance line. The rates of escape of resonance radiation predicted using these assumptions have been verified by the author[22] for the 743A line of neon for gas densities between 10^{17} and 10^{19} atom/cc.

Following Biberman we can solve Eq. (21) numerically by writing the integral equation as a system of q algebraic equations.[33] Thus,

$$\nu_r n_0 e^{\alpha x_i} = (\lambda+G)n_r(x_i) + A_r\left(n_r(x_i)-\sum_{k=1}^{q} n_r(x_k)\int_{(2m-1)d/2q}^{(2m+1)d/2q} K(|x|)dx\right), \quad (22)$$

where $x_i=(2i+1)d/2q$ and $m=|k-i|$. This can be written as

$$p_i=(\lambda+G)R_i/A_I+\sum_{k=1}^{q}\theta_m R_k, \quad 0\le i\le q, \quad (23)$$

where $p_i=\exp(\alpha d/q)^{i-\frac{1}{2}}$,

$$R_i=\frac{A_I n_r(x_i)}{\nu_r n_0}, \quad A_I=A_r(4/3\pi)(\lambda_0/3d)^{\frac{1}{2}},$$

$$\theta_{\substack{m\\ m\neq 0}}=-\frac{A_r}{A_I}\int_{2(m-1)d/2q}^{(2m+1)d/2q}K(|y|)dy = -\left(\frac{q}{8}\right)^{\frac{1}{2}}\left(\frac{1}{(2m-1)^{\frac{1}{2}}}-\frac{1}{(2m+1)^{\frac{1}{2}}}\right),$$

and

$$\theta_0=\frac{A_r}{A_I}\left(1-\int_{-d/2q}^{d/2q}K(|y|)dy\right) = \frac{2A_r}{A_I}\int_{d/2q}^{\infty}K(|y|)dy=\left(\frac{q}{2}\right)^{\frac{1}{2}}.$$

In calculating θ_0, the fact that the integral of $K(|y|)$ over all y is unity is used to evaluate the difference between the two large terms representing the photon emission and absorption in the region within $d/2q$ of x_i.[34] Note that A_I is the frequency of destruction of resonance atoms by radiation to the wall obtained by Holstein for a uniform density of resonance atoms and for a resonance line whose effective spectral distribution is determined by the dipole-dipole interaction.[13] A_I is independent of the gas density and varies only as the inverse square root of the electrode separation.

The solution to Eqs. (23) give values of R at q points separated by a distance of d/q starting at $x=d/2q$ and ending at $x=d-d/2q$. According to Eqs. (23), a different set of R_i values is obtained for each set of αd and $(\lambda+G)/A_I$ values. Typical results of the numerical solution to Eqs. (23) for $q=20$ are shown in Fig. 1. Here we have plotted $A_I n_r(x)/\nu_r n_0$ as a function of x/d for $\alpha d=6$ and various values of $(\lambda+G)/A_I$. A value

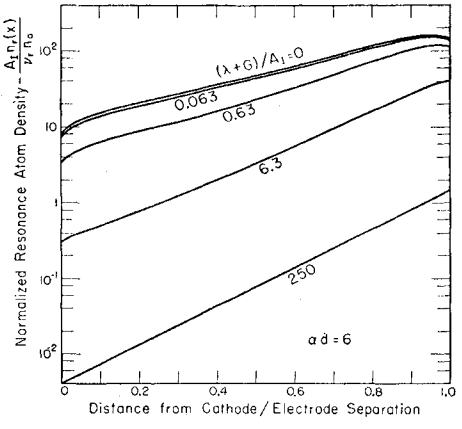

FIG. 1. Normalized resonance atom density as a function of distance from cathode for various values of $(\lambda+G)/A_I$ and for $\alpha d=6$. The upper four curves are the result of the numerical calculations. The lowest curve is calculated from Eq. (21) by neglecting the radiation terms, i.e., terms containing A_r.

[33] For the solution of a somewhat similar problem under conditions such that the escape of the resonance radiation is controlled by the Doppler broadened portion of the spectral line see A. V. Phelps, Phys. Rev. **110**, 1362 (1958).

[34] The physical significance of this cancellation is that the resonance radiation is absorbed and re-emitted many times ($\sim 10^3$) without traversing distances corresponding to significant changes in excited atom density. Finally, an excited atom radiates at a frequency such that the photon traverses a distance of the order of $d/2q$ before absorption.

of $(\lambda+G)/A_I=0$ corresponds to the steady-state solution for the resonance atom density in a gas in which there is no volume destruction of the resonance atoms. As $(\lambda+G)/A_I$ increases, i.e., as the growth constant or the volume losses increase, the spatial distribution of the density of resonance atoms approaches that of the electrons and the density of resonance atom decreases. As αd increases the spatial distribution of the resonance atom density becomes a more rapidly increasing function of x/d.

The ratio of the current density of resonance photons arriving at the cathode to the current density of electrons leaving the cathode is found by rewriting Eq. (22) for numerical integration as

$$f_r=\frac{A_r}{A_I}\alpha_r\sum_{i=1}^{q}R_i\int_{x_i}^{\infty}K(|y|)dy=\alpha_r d\sum_{i=1}^{q}R_i\psi_i, \quad (24)$$

where $\psi_i=(8q)^{-\frac{1}{2}}(2i-1)^{-\frac{1}{2}}$. According to Eq. (24), $f_r/\alpha_r d$ is a function of the same variables as R_i, i.e., αd and $(\lambda+G)/A_I$. Since the number of resonance atoms or photons produced in the gap per electron leaving the cathode is $(\alpha_r d/\alpha d)[(\exp\alpha d)-1]$, the quantity $f_r(\alpha d/\alpha_r d)[(\exp\alpha d)-1]^{-1}$ is the fraction of the resonance photons reaching the cathode. The circles of Fig. 2 show the numerically calculated values of this fraction as a function of αd for various values of $(\lambda+G)/A_I$. For a given value of $(\lambda+G)/A_I$ the fraction decreases slowly with increasing αd, i.e., by about 40%

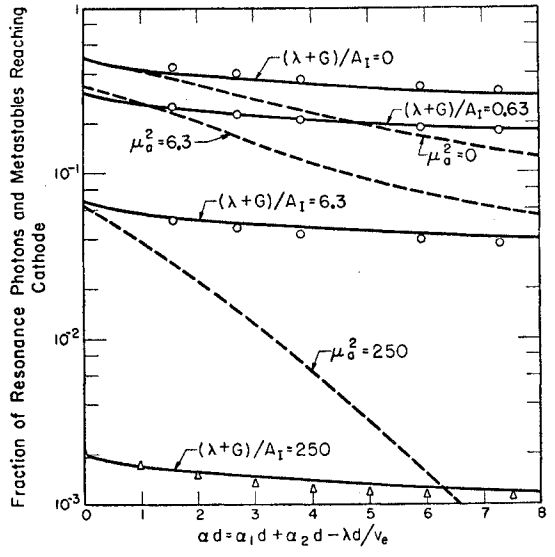

FIG. 2. Fraction of resonance photons (solid curves and open points) and metastable atoms (dashed curves) reaching the cathode as a function of αd for various values of $(\lambda+G)/A_I$ and μ_a^2. The points shown by circles (○) were calculated by numerical integration of curves such as those of Fig. 1. The points shown by triangles (△) were obtained by integrating the analytical expression for curves such as the lowest one of Fig. 1. The solid curves show the empirical expressions for the fraction of resonance photons reaching the cathode as given by the last two terms on the right-hand side of Eq. (25).

as αd increases from 0 to 8. The points shown for $(\lambda+G)/A_I=250$ were calculated by assuming that because of the large value of $(G+\lambda)$ the resonance photons do not have time to spread an appreciable distance and the resonance atom density has the same spatial dependence as the electron density, i.e., $n_r(x)=n_r(0)e^{\alpha x}$.

Instead of tabulating values of $f_r/\alpha_r d$ or the fraction of resonance photons reaching the cathode we shall give an empirical expression good to 15% or better. This relation is

$$f_r=\frac{\alpha_r}{\alpha}(e^{\alpha d}-1)\times\frac{A_I}{2[A_I+\lambda+G]}\times\frac{1}{[1+0.175(\alpha d)^{\frac{3}{4}}]}. \quad (25)$$

The right-hand side of Eq. (25) has been written as the product of three factors. The first of these is the number of atoms in the resonance state produced in the gap per electron leaving the cathode. It is the product of the ratio of resonance atom production per centimeter to the ion production per centimeter and the number of ions produced in the gap per electron leaving the cathode. To a good approximation the second factor is the fraction of resonance photons produced in the gap which reach the cathode when the resonance atom density is uniform throughout the gap, i.e., when $\alpha d=0$. This factor is identical to that expected for nonresonance photons originating from an excited state having a radiative transition probability equal to A_I and a volume destruction frequency equal to G.[35] The third factor is the reduction in the current of resonance photons reaching the cathode as the result of preferential scattering of photons to the anode. This factor varies from 1 for $\alpha d=0$ to about 0.6 for $\alpha d=8$. Thus, we find that the current of resonance photons is between 60 and 100% of that which would reach the cathode due to radiation from a nonresonance state having a transition probability equal to A_I. The solid curves of Fig. 2 show plots of the last two terms of Eq. (25) for the same parameters as the numerical calculations.

If the resonance atoms are de-excited to a lower excited state, such as a metastable state, by radiation or by collision with a ground-state atom then one needs to calculate the rate of arrival of metastable atoms or collision induced photons at the cathode due to this source. If diffusion were the dominant destruction mechanism for atoms in this lower state it would be necessary to analyze the resonance atom density distribution into Fourier components and use the result as a source term for Eq. (4). We do not perform this analysis since it would be rather difficult and since we shall make use of the theory at high pressures where the diffusion of the metastable atoms is negligible

[35] Thus, the first two terms of Eq. (25) are identical with Eq. (19) if we let $\alpha_a=\alpha_r$, $B_a=A_I$, and $C_{am}=G$. The fit of the empirical equation to the numerical calculations can be made better than 5% for $\alpha d>1.5$ by replacing A_I by $A_I/1.2$ and the factor of 2 by 1.84.

compared to the destruction by collisions.[21] Thus, Eq. (4) becomes

$$(\lambda+B_a+C_{am})n_a(x)=Gn_r(x),$$

so that

$$f_{rap}=\frac{B_a}{2(B_a+C_{am}+\lambda)}A_{rm}\int_0^d n_r(x)dx$$
$$=\frac{B_aA_p\alpha_r d}{2(B_a+C_{am}+\lambda)A_I}\frac{1}{q}\sum_{i=1}^{q}R_i.$$

Using the values of R_i found previously $\sum R_i$ can be calculated as a function of αd and $(\lambda+G)A_I$. Empirically, it is found that to within 7% of f_{rap} is given by the expression

$$f_{rap}=\frac{B_a}{2(B_a+C_{am}+\lambda)}\times\frac{A_{rm}}{(G+A_I+\lambda)}\times\frac{\alpha_r}{\alpha}(e^{\alpha d}-1). \quad (26)$$

The first of the three terms on the right-hand side of Eq. (26) is the fraction of metastable atoms which become nonresonance photons and reach the cathode. The second term is the fraction of the atoms excited to the resonance state which reach the metastable state as the result of collisions or radiation as calculated assuming that the only effect of imprisonment is to reduce the transition probability of the resonance state from A_r to A_I. The third factor is the number of resonance atoms produced in the gap per electron leaving the cathode. Thus, so far as the volume destruction of resonance atoms at high pressures is concerned, the effect of imprisonment is to a good approximation equivalent to replacing the natural transition probability, A_r, by an imprisonment transition probability, A_I.

If the separation between the energy levels of the metastable and resonance states is small enough, it is necessary to take into account the possibility that the atoms in the metastable state will be excited to the resonance state in collisions with ground-state atoms. Thus, studies of the decay of density of excited neon atoms[22] in the $^3P_2$ and $^3P_1$ state during the afterglow of a pulsed discharge show that we should add the terms $bB_an_r(x)$ and $B_an_a(x)$ to the right-hand sides of Eqs. (4) and (6), respectively. The term $Gn_r(x)$ of Eq. (6) should be replaced by $bB_an_r(x)$. Here b is the ratio of the frequency of resonance atom destruction to the frequency of resonance atom production, B_a. The ratio b is given by the theory of detailed balancing and, for example, is 1.67 exp $(601/T)$ for the $^3P_2$-$^3P_1$ transition of neon.[22] We have been able to obtain a solution for this pair of equations only in the limits of (a) low enough gas density such that the coupling terms are negligible and the metastable atoms and resonance photons reach the walls independently or (b) high enough gas density such that the diffusion of the metastable atoms to the electrodes is negligible. At low densities the solutions are as given above. In the limit of high densities the omission of the diffusion term in Eq. (4) allows one to solve Eq. (4) for $n_a(x)$ and then eliminate $n_a(x)$ from Eq. (6). The new form of Eq. (6) is then identical with the old form if we replace ν_r by $\nu_r+\nu_a[1+(\lambda+C_{am})/B_a]^{-1}$ and G by $bB_a[1+B_a/(\lambda+C_{am})]^{-1}$. Using these substitutions, the number of resonance photons reaching the cathode per electron leaving, f_r, can be found from the empirical equation, Eq. (25).

At this point it is appropriate to emphasize the fact that the behavior of imprisoned resonance radiation is much different from that of the diffusing metastable atoms and that the imprisonment of resonance radiation cannot be described by ordinary diffusion theory.[7] First, we note that the parameter λ/A_I of the imprisonment solution is independent of the gas density and varies only as the square root of the separation of the electrodes, whereas the parameter λNd^2D_a of the diffusion theory is proportional to the density and to the square of the electrode separation. Secondly, the results of our calculations show that the fraction of metastable atoms reaching the cathode, the dashed curves of Fig. 2, depends much more strongly upon αd than does the fraction of the resonance photons reaching the cathode, the solid curves of Fig. 2. Thus, for a static discharge ($\lambda=0$) and no volume destruction ($G=B_a=C_{am}=0$) the fraction of metastable atoms reaching the cathode decreases from 0.5 to 0.125 as αd varies from 0 to 8 while the fraction of resonance photons reaching the cathode decreases 0.5 to 0.3 for the same variation in αd. For large $(\lambda+B_a+C_{am})Nd^2/D_a$ the variation of the metastable fraction, f_a, decreases exponentially with αd whereas the dependence of the resonance photon fraction on αd is essentially unchanged from that for $(\lambda+G)/A_I=0$.

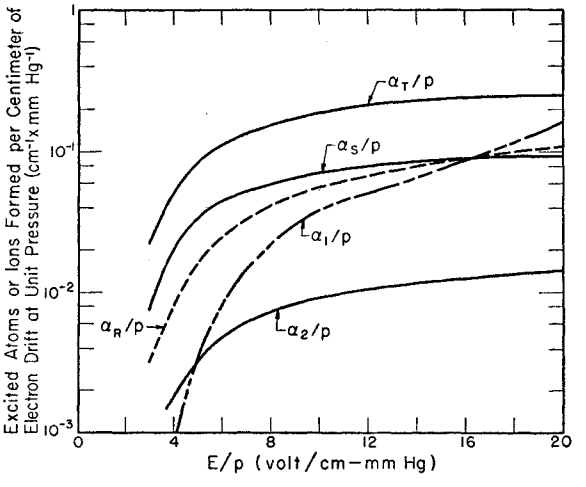

FIG. 3. Townsend ionization and excitation coefficients for helium at high gas densities as a function of E/p at 300°K. This data can be used at other gas temperatures by considering p to be a unit of gas density equal to 3.22×10^{16} atom/cc. As discussed in the text this data is not applicable at low gas densities or very large λ.

IV. APPLICATION OF THEORY

In this section we will attempt to give our theoretical formulas more meaning by applying them to a calculation of the growth constant, λ, as a function of the applied voltage, V, for typical experimental conditions. First we consider pure helium and then helium with a very small admixture of neon.

A. Pure Helium

Helium is probably the best gas in which to test theories of breakdown since more is known about the behavior of electrons and excited atoms in helium than in any other gas. Thus, the cross sections for the elastic scattering of electrons and for the excitation and ionization of helium by electrons have been determined.[15,17,36] These have been used to calculate electron energy distribution functions, ionization frequencies, and excitation frequencies at various values of E/p (electric field to pressure ratio) for comparison with experiment. Electron and ion drift velocities have been measured.[18,19,37] The diffusion coefficients, two-body and three body collision coefficients have been measured for helium atoms and molecules in the metastable states.[19] Theoretical calculations have been made of the transition probabilities for the various radiative transitions and a few of the values have been checked by experiment.[36] Some of the frequencies of excitation transfer have been measured so that one can make estimates of the effect of this process on the net excitation rates.[36]

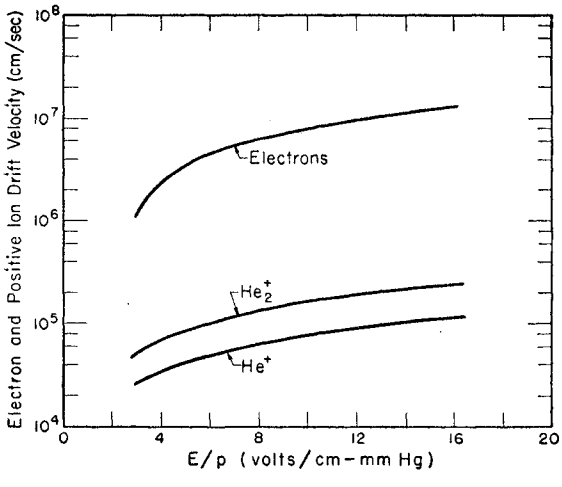

FIG. 4. Electron and ion drift velocities as a function of E/p at 300°K. The electron drift velocity data can be used at other temperatures by regarding p as a unit of gas density equal to 3.22×10^{16} atom/cc.

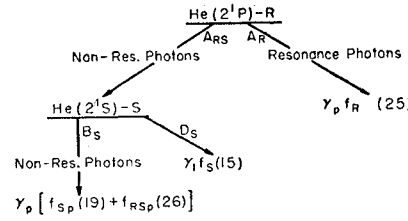

FIG. 5. Schematic of processes leading to the arrival of singlet metastable atoms and resonance and nonresonance photons at the cathode during the buildup of current preceding breakdown in helium. The horizontal lines represent excited states while diagonal lines represent processes characterized by the coefficients such as the transition probability, A_R, for the emission of resonance radiation by the 2^1P resonance (R) state. The $\gamma_n f_n$ products at the ends of the arrows are the fractions of the cathode current resulting from the arrival of the species designated by the final subscript and originating at a state indicated by the initial subscript. The equation used to evaluate the $\gamma_n f_n$ value is indicated in parenthesis.

An immediate simplification of the theory as applied to helium is that for $\lambda<10^7$ sec^{-1} and gas densities greater than 10^{17} atoms/cc the effects of the imprisonment of resonance radiation and the transfer of excitation are large enough so that the only resonance photons which can reach the electrodes in significant numbers are those from the 2^1P state. In the notation[38] of Sec. III this means that for the n^1P states with $n\geq3$, $G>\lambda$ and $G/A_I\gg1$ so that none of the excitation to the higher n^1P states reaches the electrodes but instead is divided among the metastable states and lowest resonance (2^1P) state. As a result, for a given E/p, the rates of production of resonance and metastable atoms per electron are independent of gas density, growth constant, and electrode spacing. Figure 3 shows the variation with E/p of the excitation coefficients and the Townsend ionization coefficients for the production of atomic and molecular ions. Figure 4 shows the electron and positive ion drift velocities as a function of E/p. The processes leading to the arrival of photons or metastable atoms at the cathode are indicated in Figs. 5 and 6. Values of the various associated coefficients are listed in Table II for an arbitrary gas density. The important λ dependent parameters of the theory are listed in Table III for $d=1$ cm and a gas pressure of 100 mm Hg at 300°K.

The number of atomic and molecular positive ions arriving at the cathode per electron leaving is calculated by substituting the values of α_1, α_2, v_e, v_1, and v_2 from

[36] L. S. Frost and A. V. Phelps (to be published.) Similar results have been obtained by S. J. B. Corrigan and A. von Engel, Proc. Phys. Soc. (London) 72, 786 (1958). Although these authors obtain shapes of the excitation cross-section curves for the various excited shapes of helium which differ significantly from those of Frost and Phelps, the ionization and total excitation frequencies are in satisfactory agreement.

[37] Phelps, Pack, and Frost, Phys. Rev. 117, 470 (1960).

[38] Here G is the sum of (a) the transition probabilities per unit time for all radiative transitions except the transitions to the ground state (resonance transitions) and (b) the net frequencies of transfer of excitation to other states such as n^1D and n^3D. The helium densities of interest are high enough such that one expects the density of atoms in the n^1P state relative to the densities of atoms in the corresponding n^1D, n^3D, etc., states to be given by detailed balancing. Also, one expects the net n^1P destruction frequency by excitation transfer to be determined primarily by the radiative transition probabilities for the n^1D, n^3D, etc., states. See reference 15, Chap. VII, Sec. 8.2 and reference 33.

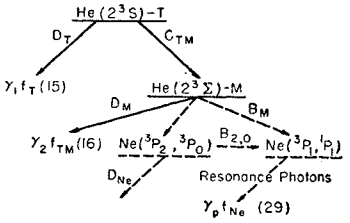

FIG. 6. Schematic of processes leading to the arrival of triplet metastable atoms and molecules at the cathode. The meaning at the symbols and lines is the same as for Fig. 5. The dashed lines indicate the additional processes introduced by the presence of small concentrations of neon.

Figs. 3 and 4 and the value of C_{12} from Table III into Eqs. (12) and (13). Figure 5 shows that atoms excited to the resonance (2^1P) state either emit resonance photons or emit infrared photons in a radiative transition to the singlet metastable (2^1S) state. Figure 5 also shows that the radiative transition probabilities for the emission of the resonance photon and nonresonance photon are A_R and A_{RS}, respectively, so that in this case $G=A_{RS}$. The number of resonance photons arriving at the cathode per electron leaving, f_R, is to be calculated using Eq. (23). According to Table III a value of $\lambda=2\times10^6$ sec^{-1} is required to increase $(A_{RS}+\lambda)/A_I$ by a factor of two so that at a given E/p we expect f_R to be nearly independent of λ for $\lambda<10^6$ sec^{-1}.

Figure 5 shows that atoms may be excited to the singlet metastable (2^1S) state by radiative transitions from the 2^1P resonance state as well as by direct excitation and by radiation from higher n^1P states. The singlet metastable atoms may diffuse to the cathode as metastables with a diffusion coefficient D_S or may be converted into nonresonance photons as a result of collisions with ground-state atoms at a frequency, B_S. According to Table III, the conditions of our example are such that $\mu_S^2\gg1$ and, since $\alpha d<6$, $\mu_S^2\gg\alpha^2d^2$ so that the number of singlet metastable atoms reaching the cathode per electron leaving, f_S, is given by the limiting form of Eq. (12), $f_S=\alpha_S d/(\mu_S-\alpha d)$ and is expected to be small for all λ. The contribution to the cathode current due to the arrival by diffusion of singlet metastables which were originally formed as resonance atoms is smaller than f_S and is neglected. Figure 5 shows that the number of nonresonance photons reaching the cathode per electron leaving, $f_{Sp}+f_{RSp}$, is found using Eqs. (16) and (24). Since Eqs. (16) and (24) depend upon λ through the ratio λ/B_S, the contribution of nonresonance photons from the 2^1S state will decrease rapidly for $\lambda>2\times10^4$ sec^{-1}.

Figure 6 shows that atoms excited to the triplet metastable (2^3S) state may diffuse to the cathode with a diffusion coefficient D_T or be converted into metastable ($2^3\Sigma$) molecules in three-body collisions at a frequency, C_{TM}. The data of Table III show that for the conditions of our example, $\mu_T^2\gg1$ and $\mu_T^2\gg\alpha^2d^2$ so that the number of triplet metastable atoms arriving at the cathode per electron leaving is small and is given by the limiting form of Eq. (12), $f_T=\alpha_T d/(\mu_T-\alpha d)$. If the helium used in a breakdown measurement is extremely pure, then the metastable ($2^3\Sigma$) molecules appear to be destroyed only as a result of diffusion to the electrodes.[21] The number of metastables arriving at the cathode per electron leaving is then given by the limiting form of Eq. (13) for $\mu_a^2\gg1$ and $\mu_a^2\gg\alpha^2d^2$, i.e., the right-hand side of Eq. (12) with α_a and μ_a replaced by α_T and μ_M and multiplied by $(1+\lambda/C_{TM})^{-1}$. From Table III we see that $\mu_M=1$ for $\lambda=3.1$ sec^{-1} so that we expect f_{TM} to be significant only at very small λ.

In order to find the applied voltage which will yield a given value of λ we need to consider the boundary condition on the electron current given in Eq. (6). This

TABLE II. Coefficients governing current buildup in helium at 300°K.

State and process	Symbol	Value
He^+ to He_2^+ conversion	C_{12}	$6\times10^{-32}N^2$ sec^{-1}
2^1P resonance transition probability	A_R	1.8×10^9 sec^{-1}
2^1P imprisonment constant	A_I	$1.06\times10^6(d)^{-\frac{1}{2}}$ sec^{-1}
2^1P-2^1S transition probability	A_{RS}	2.0×10^6 sec^{-1}
2^1S diffusion coefficient	D_S	1.4×10^{19} cm^{-1} sec^{-1}
2^1S collision induced radiation	B_S	$6\times10^{-15}N$ sec^{-1}
2^1S three-body destruction	C_{SN}	$<10^{-32}N^2$ sec^{-1}
2^3S diffusion coefficient	D_T	1.51×10^{19} cm^{-1} sec^{-1}
2^3S three-body collision	C_{TM}	$2.5\times10^{-34}N^2$ sec^{-1}
2^3S collision induced radiation	B_T	$<2\times10^{-17}N$ sec^{-1}
$2^3\Sigma$ molecular metastable diffusion	D_M	1×10^{19} cm^{-1} sec^{-1}
$2^3\Sigma$ destruction by neon	$B_M=\Sigma B_{Mj}$	$3\times10^{-11}cN$ sec^{-1}
$Ne(^3P_1)$ resonance transition probability	$A_r(^3P_1)$	6.2×10^7 sec^{-1}
$Ne(^3P_1)$ imprisonment of resonance radiation	$A_I(^3P_1)$	$\approx3\times10^4(cd)^{-\frac{1}{2}}$ sec^{-1}
$Ne(^3P_0)$ de-excitation to $^3P_1$ state by helium	B_0	$4\times10^{-15}N$ sec^{-1}
$Ne(^3P_2)$ excitation to $^3P_1$ state by helium	B_2	$2\times10^{-14}N$ sec^{-1}
$Ne(^3P_2)$ three-body destruction	$C(^3P_2)$	$\approx5\times10^{-34}cN^2$ sec^{-1}
$Ne(^3P_2)$ diffusion coefficient	D_{Ne}	2×10^{19} cm^{-1} sec^{-1}
$Ne(^3P_2)$ elastic collision frequency in helium	ν_c	$4\times10^{-10}N$ sec^{-1}
Helium density	N	
Fractional neon density	c	$c\ll1$

condition can be written in the form

$$\gamma_1(f_T+f_S+f_1)+\gamma_2(f_2+f_M)+\gamma_p(f_{RSp}+f_{Sp}+f_R)=1. \quad (27)$$

Here we have assumed that the yield of electrons due to helium atomic ions and helium singlet and triplet metastable atoms are the same.[39] The electron yield for the helium molecular ion and metastable molecule is expected to be about 40% lower than the value for the atomic ions and metastables.[39] The energies of the resonance and nonresonance photons are nearly the same and are assumed to produce the same yield of electrons at the cathode.

We have chosen gold as the cathode surface for our example since it appears to be a relatively stable surface and is easily prepared experimentally. The yields used in the calculation are: 0.3 for the atomic ions and metastable atoms,[40] 0.2 for the molecular ions and metastable molecules,[39] and 0.05 for the photons.[26]

TABLE III. Parameters of imprisonment and diffusion equations for $d=1$ cm, $N=3.22\times10^{18}$ atom/cc ($p=100$ mm), and 300°K.

Symbol	Value (λ in sec^{-1})
C_{12}	6×10^5 second^{-1}
$(A_{RS}+\lambda)/A_I$	$1.9+9.4\times10^{-7}\lambda$
$\mu_S^2=(B_S+\lambda)Nd^2/D_S$	$4.5\times10^3+0.23\lambda$
λ/B_S	$5.2\times10^{-5}\lambda$
$\mu_T^2=(C_{TM}+\lambda)Nd^2/D_T$	$550+0.21\lambda$
λ/C_{TM}	$3.8\times10^{-4}\lambda$
Pure He	
$\mu_M^2=\lambda Nd^2/D_M$	0.32λ
He+2×10^{-5}Ne	
$\mu_M^2=(B_M+\lambda)Nd^2/D_M$	$620+0.32\lambda$
λ/B_M	$5.0\times10^{-4}\lambda$
$\mu_{Ne}^2=(bB_2+\lambda)Nd^2/D_{Ne}$	$6\times10^4+0.17\lambda$
$\lambda/A_I(^3P_1)$	$1.4\times10^{-7}\lambda$
λ/B_2	$1.55\times10^{-5}\lambda$
λ/B_0	$1.3\times10^{-3}\lambda$

These values must be multiplied by a factor which takes into account the effects of scattering of the emitted electrons back to the cathode as a result of collisions with gas atoms. Since we do not know of any measurements of this quantity for electrons in helium we shall assume a typical value of 0.3 and neglect its variation with E/p and the initial energy of the electrons emitted from the cathode. The resultant values of γ are: $\gamma_1=0.09$, $\gamma_2=0.06$, and $\gamma_p=0.015$. The calculations are carried out by calculating $\sum\gamma_n f_n$ at integral values of $\alpha_i d$ for an assumed λ and using an exponential interpolation to find the value of $\alpha_i d$ and V, which makes $\sum\gamma_n f_n=1$.

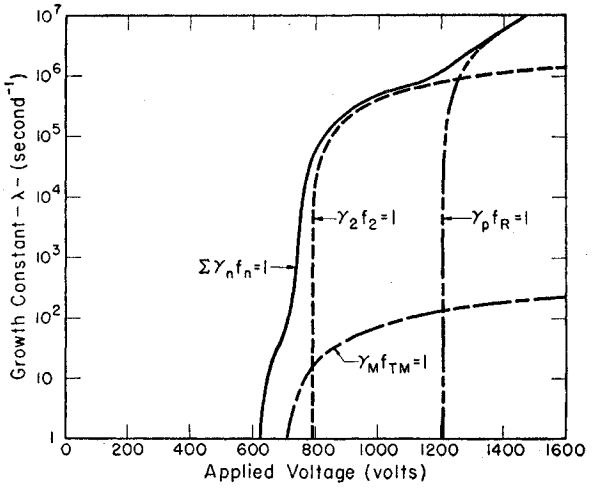

FIG. 7. Predicted growth constant as a function of applied voltage for 100 mm Hg of helium at 300°K with infinite parallel plane electrodes and a gold cathode. The solid curve is calculated assuming all processes contribute to the cathode current and is the curve which should be observed experimentally. The dashed curves labeled, $\gamma_{TM}f_M=1$, $\gamma_2 f_2=1$, and $\gamma_p f_R=1$ show the expected variation of λ with V if only the molecular metastables, molecular ions, or resonance photons contributed to the cathode current.

The calculated values of λ as a function of the amplitude of the voltage pulse applied to the gap are shown by the solid curve of Fig. 7, while the fraction of the electron current leaving the cathode for each secondary process, $\gamma_n f_n$, is given in Fig. 8 as a function of λ. From Fig. 8 one sees that the principal source of cathode current at low values of λ is the emission of electrons resulting from the arrival of molecular metastables at the cathode, i.e., $\gamma_2 f_{TM}$. At intermediate values of λ the contribution due to molecular ions, $\gamma_2 f_2$, dominates, while at the largest λ the production of electrons due to the arrival of resonance radiation, $\gamma_p f_R$, is the most important process.

The roles of the various secondary processes in determining the shape of the λ as V curve is shown by the dashed curves of Fig. 7. Thus, the curve labeled

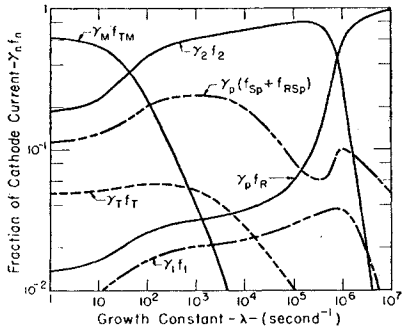

FIG. 8. Fraction of cathode current contributed by various secondary processes as a function of the growth constant.

[39] H. G. Hagstrum, Phys. Rev. **91**, 543 (1953); and L. J. Varnerin, Phys. Rev. **91**, 859 (1953). These papers show that if the work function of the metal surface is sufficiently large compared to the energy required to ionize the metastable atom or molecule, the metastable atoms or molecules will be ionized as they approach the surface and the electron yield will be the same as for the corresponding positive ion. See J. P. Molnar, reference 24, for experimental evidence for the equality of the electron yields due to argon ions and metastable atoms. We have taken the yield for the molecular ion to be approximately two-thirds of that for the atomic ion as found by Hagstrum for gas covered tantalum.

[40] J. B. Hasted, J. Appl. Phys. **30**, 22 (1959).

$\gamma_2 f_{TM}=1$ is calculated by setting $f_{TM}=1/\gamma_2$ and finding the value V necessary to give a desired λ. This is equivalent to assuming that the yields due to all other secondary processes are zero. From this calculation we see that the knee of the λ *vs* V curve at $\lambda\sim 10$ sec^{-1} corresponds to the knee of the $\gamma_2 f_{TM}=1$ curve. Examination of Eq. (16) and of the constants of Table III shows that these knees occur when the time required for a metastable molecule to diffuse across the gap is of the order of the time, $1/\lambda$, required for the current to increase by 2.7. As far as their contribution to the cathode current is concerned, the metastable molecules which remain in the gap during the buildup are as ineffective as if destroyed by some volume process characterized by a destruction frequency λ. This equivalence of destruction and buildup of density in the gap is also seen in the differential equation for the metastable density, e.g., Eq. (14) for the atomic metastables contains the sum of the volume destruction frequencies and the growth constant.

The curve labeled $\gamma_2 f_2=1$ in Fig. 7 shows variation of λ with V expected if only the molecular ions were capable of releasing electrons from the cathode. Here we see that the molecular ions are the principal factor in determining the shape of the λ *vs* V curve for intermediate λ. In this case, the knees of the λ curves at $\lambda\sim 10^5$ sec^{-1} result when the time required for the ions to cross the gap becomes comparable with $1/\lambda$ and the ions begin to remain in the gap. Similarly, the $\gamma_p f_R=1$ curve assumes that only resonance photons release electrons at the cathode. The closeness of this curve and the $\sum\gamma_n f_n=1$ curve at large λ again shows that the resonance radiation is the principal source of cathode current at λ near 10^7 sec^{-1}.

Figure 8 shows that the contribution of collision induced radiation $\gamma_p(f_{Sp}+f_{RSp})$, to the cathode current varies from 5 to 25%. The detailed calculations show that about 40% of the singlet metastables, which are the source of the collision-induced radiation, arrive at the singlet metastable state by radiative decay from the resonance state. Also, the calculations show that the fraction of the molecular ions reaching the cathode which were formed from atomic ions by three-body collisions varies from 70% at small λ to 35% at $\lambda\sim 10^5$ sec^{-1}. Figure 8 shows that at the pressure and gap spacing of our example, the contributions to the cathode current of electrons produced from atomic metastables and atomic ions arriving at the cathode are less than 6% of the total, and, therefore, essentially negligible.

The effect of changing the helium density or electrode spacing is most easily seen by considering the changes in the λ *vs* V curves for the dominant process contributing to the cathode current. Examination of the appropriate equations shows that in general none of the dominant processes in our example can be characterized by the usual three proper variables[1] of λd, V, and Nd (or pd at constant temperature). Thus, we cannot regard the λ *vs* V curve of Fig. 7 as a λd *vs* V curve which will apply over wide ranges of gas density so long as Nd has the value chosen for our example. This failure of three variables to completely characterize the results is due to the presence of the three-body coefficients in the equations corresponding to the contributions of metastable molecules and molecular ions and to the dependence of the imprisonment constant, A_I, on the square root of the electrode separation.

B. Helium with Neon Impurity

If the helium used in the breakdown measurements contains small concentrations of impurities, the operation of a glow discharge or the repeated application of breakdown voltages will drive most of the impurity atoms into the cathode as positive ions.[41] However, neon is not removed efficiently by this process so that most samples of helium contain small concentrations of neon, e.g., two parts in 10^5 of neon for high purity commercial helium.[21] As shown by Fig. 6, this concentration of neon can result in the transfer of the helium $2^3\Sigma$ molecular metastable energy to the states of the $2p^5 3s$ configuration of neon at a frequency of B_M sec^{-1}. Figure 6 also shows that excited neon atoms found in the $^3P_1$ and $^1P_1$ states may either emit neon resonance radiation or be converted into $^3P_2$ or $^3P_0$ atoms upon collisions with ground state atoms.[22] Excited atoms formed in the $^3P_2$ or $^3P_0$ states may diffuse to the electrodes, be destroyed in three-body collisions with ground-state atoms, or be converted into $^3P_1$ or $^1P_1$ states.[22] Although the rates of diffusion, conversion, and three-body processes are known with sufficient accuracy, we cannot obtain a general solution of our problem because of a lack of knowledge as to the relative ratio of production of the states of the $2p^5 3s$ configuration and because we have not solved the coupled equations at low gas densities where diffusion of the metastable atoms to the electrodes is an important process.

For helium densities equal to or greater than that of our example diffusion effects are negligible and important simplifications occur in the solutions of the coupled equations for the various states of the$2p^5 3s$ configuration. The helium densities of our example are expected to be more than that required for the escape of the neon resonance radiation to be controlled by the collision broadening of the resonance lines as described in Sec. III. Since we have no theoretical or experimental information as to the frequency of collisions causing significant perturbations of the radiating neon atoms, we shall use the elastic collision frequency computed from the diffusion coefficient for neon metastables in helium.[22,26] This collision frequency, ν_c, is shown in Table II and is used to calculate the line breadth using relations given by Mitchell and Zemansky[26] and the imprisonment constant shown, A_I, according to equations given by Holstein.[13] For the conditions of our

[41] A. Riesz and G. H. Dieke, J. Appl. Phys. **25**, 196 (1954).

example $A_I(^3P_1)$ is equal to 7×10^6 sec^{-1} compared to 1×10^6 sec^{-1} for the helium resonance line. We, therefore, expect imprisonment effects to be significantly smaller than for the helium resonance line. If we take into account the effects of transitions between the $^3P_2$, $^3P_1$, and $^3P_0$ states of the $2p^53s$ configuration according to the imprisonment theory in the presence of coupled equations given in Sec. III, we find that the effective value of the factor $[1+(\lambda+G)/A_I]^{-1}$ of Eq. (23) varies from 1.0 for $\lambda=0$ to 0.8 for $\lambda=10^6$ sec^{-1}. Accordingly, a lack of an accurate value for the frequency of line broadening collisions is not too important so long as it is not significantly smaller than our assumed value. Since the transition probability for the resonance transition originating with the $^1P_1$ state of neon (736A) is 13.2 times that for the $^3P_1$ state,[42] the effective imprisonment constant for the 736A photons is larger than that for 743A photons and its exact value is even less important.

If the theory of imprisonment in the presence of coupled equations is extended to include the two metastable states of neon, the effective frequency of neon $^3P_1$ resonance atom production, ν_r, is found to be given by

$$\nu_r=\nu(^3P_1)+\nu(^3P_2)(1+\lambda/B_2)^{-1}+\nu(^3P_0)(1+\lambda/B_0)^{-1}. \quad (28)$$

Here the ν's are the frequencies of production of the respective states, and B_2 and B_0 are the frequencies of conversion of atoms in the $^3P_2$ and $^3P_0$ states to the $^3P_1$ state as given in Tables II and III. Here we have assumed that all of the $^3P_0$ atoms are converted directly into $^3P_1$ atoms whereas actually about half are converted directly and about half by way of the $^3P_2$ state.[22] Because of the large value of $A_I(^3P_1)$ the effect of this assumption on ν_r is negligible. Since diffusion effects are assumed to be negligible, the frequencies of production of the various excited neon atoms are equal to the frequency of helium molecular metastable production times a factor of the form $(1+\lambda/B_{Mj})^{-1}$, where B_{Mj} is the frequency of transfer of excitation from the molecular metastable state to the state of the neon $2p^53s$ configuration with a total angular momentum of j. The ratio of the frequency of helium molecular metastable production to the frequency of helium triplet atomic metastable production, ν_T, is $(1+\lambda/C_{TM})^{-1}$.

Our lack of knowledge of the relative values of the B_{Mj} prevents effective use of Eq. (28). However, from Table III we see that λ/B_0 and λ/B_2 are significantly smaller than λ/C_{TM} and λ/B_M so that the contribution of the neon resonance radiation to the cathode current will be small when the λ/B_0 and λ/B_2 ratios in Eq. (28) are comparable with unity. This means that to a good approximation we can assume that neon atoms formed in the $^3P_2$ and $^3P_0$ states are converted into $^3P_1$ atoms with negligible delay. Furthermore, because of the large values of A_I for both resonance states compared to the λ values of importance in this calculation ($\lambda<10^4$ sec^{-1}), we can assume that all of the excited neon atoms are formed in a single resonance state. Thus, the contribution of neon resonance radiation is given by

$$f_{\mathrm{Ne}}=\frac{1}{(1+\lambda/C_{TM})(1+\lambda/B_M)}\frac{1}{[1+0.175(\alpha d)^{\frac{3}{4}}]}\times\frac{\alpha_T}{\alpha}(e^{\alpha d}-1). \quad (29)$$

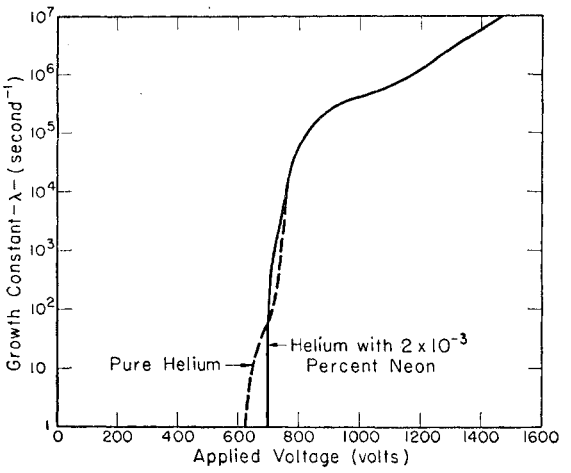

FIG. 9. Growth constant as a function of applied voltage for pure helium (dashed curve) and for helium containing 2×10^{-3}% neon (solid curve).

The dashed curve of Fig. 9 shows the calculated effect of conversion of helium metastable molecules into neon excited atoms and then into resonance photons for the conditions of our example. The yield of electrons per neon resonance photon striking the cathode was assumed to be the same as for helium photons. Thus, the effect of the 2×10^{-5} parts of neon is to raise the voltage required to make $\lambda=1$ sec^{-1} from about 625 volts to about 700 volts and effectively eliminate the "knee" attributed to the helium metastable molecules. The calculations show that the presence of the neon reduces the contribution of the molecular metastables, $\gamma_2 f_{TM}$, by a factor of 10 from its pure helium value. A slight knee appears at $\lambda\approx10^3$ sec^{-1} and is due to the decreasing contribution of the neon resonance radiation to the cathode current.

V. DISCUSSION

The preceding analysis shows that it is possible to make detailed predictions of the growth constant *vs* voltage characteristics for a rare gas for which the ionization and excitation probabilities, the interactions

[42] G. H. Shortley, Phys. Rev. 47, 295 (1935). Recently, A. Gold and R. S. Knox, Phys. Rev. 113, 834 (1959) have obtained theoretical values for the radiative transition probabilities for the 3^1P_1 and 3^3P_1 states of neon which are about a factor of two smaller than the values given in reference 22.

of electrons, ions, and excited atoms with ground-state atoms, and the electron yields due to ions, excited atoms, and photons are known. At present the only gas for which this information is available is helium. Even in the case of helium, our knowledge of such processes as molecular ion formation from highly excited atoms and the net yield of electrons from cathode surfaces is unsatisfactory and constitutes a possible source of significant error in our calculation.

Our conclusion that the net effect of resonance radiation can be described in much the same manner as the effect of delayed nonresonance photons is one more example of the fact that the transport of resonance radiation cannot be treated properly using conventional diffusion theory. Thus, the time constant characteristic of the resonance radiation, $1/A_I$, varies as the square root of the electrode separation and is independent of gas density while the time constant characteristic of conventional diffusion, Nd^2/D_a, is directly proportional to the gas density and to the square of the electrode separation.

Two outstanding features of the analysis presented in this paper are the complexity of the problem and the fact that none of the processes found to control the current buildup in helium are the simple processes involving atomic ions, atomic metastables, and nonresonance photons usually considered in the analysis of experimental data. Examination of available data as to ion and excited atom behavior in neon and argon suggests that the existence of four closely-spaced metastable and resonance states would lead to more complicated calculations than for helium. The calculations are not expected to be significantly simpler in the molecular gases except possibly in the case of hydrogen where there are no metastable molecules[15] and where the time required for the destruction of metastable atoms and for an H_2^+ ion to be converted into an H_3^+ ion[43] is believed to be very short.

VI. ACKNOWLEDGMENT

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[43] Eyering, Hirshfelder, and Taylor, J. Chem. Phys. 4, 479 (1936).

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Dynamical Theory of Diffusion in Crystals*

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Corrections to a previous paper by the second author are presented. A calculation leading to the simplification of the pair correlation functions is also presented.

THE purpose of this brief paper is twofold: to correct some errors in a previous article,[1] and to extend the utility of the theory by demonstrating a great simplification of the pair correlation function. It is to be emphasized at the outset that the errors in no way alter the physical arguments advanced by Rice or the final formulation of the diffusion coefficient.

We proceed by remarking that the dynamical theory presented previously is based on the Einstein relation

$$\mathfrak{D}=\tfrac{1}{2}\Gamma(\Delta x)^2, \tag{1}$$

with Γ the frequency of atomic jumps and Δx the length of a jump. Equation (1) is conveniently rewritten in the form

$$\mathfrak{D}=[(\Delta x)^2/2]\sum_{\text{n.n.}}\varphi\tilde{P}(\{\delta\}), \tag{2}$$

with φ the site fraction of vacancies, and $\tilde{P}(\{\delta\})$ the frequency of occurrence of a configuration in which the migrating atom has large amplitude of vibration properly oriented and there is a properly phased motion of the surrounding atoms. The summation is to be taken over all atoms that can jump into the vacancy. This usually consists of just the nearest neighbors and has been so indicated by n.n. Following the arguments

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‡ Alfred P. Sloan Fellow.

[1] S. A. Rice, Phys. Rev. 112, 804 (1958).