Diffusion, De-Excitation, and Ionization Cross Sections for Metastable Atoms. I

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The lifetimes of metastable atoms in gases are determined from studies of the ionization which they produce in the afterglow following a pulsed discharge. Two distinct types of ionizing reactions are studied, the first in which the collision of a pair of metastable atoms results in ionization of one of them and de-excitation of the other, the second in which a metastable atom of one type loses its excitation energy in ionizing a normal atom of another type. From studies of this ionization as a function of various experimental parameters such as gas pressure, we obtain values of the diffusion, de-excitation, and ionization cross sections of metastable helium and neon atoms. The various measured cross sections agree reasonably well with values obtained from modern optical absorption studies.

THE lifetime of metastable atoms in gases is determined by their diffusion to container walls and by various inelastic collision processes in the gas. Previously, metastable lifetimes have been measured by optical absorption techniques[1,2] and by studies of the current pulse shape in a Townsend discharge,[3] or estimated from studies of the Townsend ionization coefficient at breakdown of a gas.[4] In the present experiment, metastable lifetimes are measured by studies of the ionization which the metastable atoms produce in the afterglow following a pulsed discharge.[5]

I. IONIZING REACTIONS INVOLVING METASTABLE ATOMS

A number of ionizing reactions involving metastable atoms have been suggested; of these two have been studied experimentally. The first reaction, proposed by Schade and Büttner,[6] involves the collision of two metastable atoms, resulting in the ionization of one of them and the de-excitation of the other. For example,

$$\mathrm{He}^* + \mathrm{He}^* \rightarrow \mathrm{He} + \mathrm{He}^+ + e, \qquad (1)$$

where * indicates an atom excited to a metastable state and + indicates an ion. This reaction is energetically possible if the sum of the excitation energies of the metastables is equal to the ionization potential of the atom.[7]

The reaction illustrated by Eq. (1) was proposed in order to explain ionization in excess of that produced by avalanche electrons in the Townsend discharge.[8] Schade and Büttner's measurements in neon revealed a magnitude and a pressure dependence of this excess ionization which fitted the proposed reaction. However, they were unsuccessful in their attempts to demonstrate the metastable origin of this ionization by irradiation experiments;[9] therefore, their explanation was regarded as unsatisfactory. In the present experiment, we have been able to demonstrate the dependence of the observed ionization on the metastable concentration, and our data are consistent with the proposed metastable-metastable ionizing reaction.

A second ionizing reaction involving metastable atoms was studied by Penning's group at Eindhoven.[4] If a metastable atom of type 1 collides with a normal atom of type 2 and

$$V_1^* \geqslant V_2^+, \qquad (2)$$

where V_1^* is the metastable excitation potential and V_2^+ is the ionization potential, then the metastable may yield its energy in ionizing the normal atom of type 2. Using neon and argon as an example, we have

$$\mathrm{Ne}^* + \mathrm{A} \rightarrow \mathrm{Ne} + A^+ + e. \qquad (3)$$

Penning's group studied the effect of small admixtures of argon on the breakdown potential of neon. They were able to estimate a cross section for the Ne-A reaction which we shall compare with our results.

II. DIFFUSION AND DE-EXCITATION OF METASTABLE ATOMS

The ionizing processes described in the previous section are often of secondary importance in determining metastable lifetimes. Under many experimental conditions, metastable atoms are lost chiefly by diffusion to the enclosure walls (where they may lose their energy in an inelastic impact with the wall) and by de-exciting collisions with normal gas atoms.[10] The diffusion follows the usual description given in standard texts. The de-excitation collisions are of two types: those resulting in actual transfer of the metastable to a radiating state, and those which perturb the metastable atom suffici-

[1] K. W. Meissner and W. Graffunder, Ann. Physik 84, 1009 (1927).
[2] J. P. Molnar and A. V. Phelps, Phys. Rev. (to be published).
[3] J. P. Molnar, Phys. Rev. 83, 933 (1951).
[4] A. A. Kruithof and F. M. Penning, Physica 4, 430 (1937); A. A. Kruithof and M. J. Druyvestyn, Physica 4, 450 (1937).
[5] M. A. Biondi, Phys. Rev. 82, 453 (1951); 83, 653 (1951).
[6] R. Schade, Z. Physik 105, 595 (1937); 108, 353 (1938); H. Büttner, Z. Physik 111, 750 (1939).
[7] An alternate reaction, in which two metastable atoms collide to produce a molecular ion, is also possible. We found no evidence of such formation of molecular ions in our experiments and hence shall neglect such a process in this paper.
[8] See, for example, M. J. Druyvestyn and F. M. Penning, Revs. Modern Phys. 12, 87 (1940).
[9] See Sec. V.
[10] A. C. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, Cambridge, 1934), p. 245 ff.

ently to break the optical selection rule (collision-induced radiation).[11] The probability for these de-exciting collisions depends on the energy of the colliding particles and the separation between the metastable level and nearby radiating states of the atom. Quantitative calculations of the cross sections are not possible since detailed information concerning the potential energy curves for these reactions is not available at present.

III. EQUATIONS GOVERNING THE METASTABLE ATOM CONCENTRATION AND THE ELECTRON DENSITY

In the following sections, we shall consider only those processes discussed in Secs. I and II as significant in determining the metastable decay; that is, we shall neglect processes such as inelastic collisions between metastable atoms and electrons. Consequently, the differential equation governing the rate of change of metastable concentration is

$$\partial M/\partial t = D_m \nabla^2 M - \nu_d M - \nu_i M - \alpha_I M^2, \tag{4}$$

where M is the metastable atom concentration, D_m the metastable diffusion coefficient, ν_d the frequency of de-excitation, ν_i the frequency of ionization for reactions of the type illustrated by Eq. (3), and α_I is the ionization frequency per unit metastable concentration for the reaction given by Eq. (1). The de-excitation and ionizing rates are related to the appropriate cross sections σ by

$$\nu_d = n_g \bar{v}_1 \sigma_d, \tag{5}$$

$$\nu_i = n_a \bar{v}_2 \sigma_i, \tag{6}$$

$$\alpha_I = \bar{v}_3 \sigma_I, \tag{7}$$

where n_g is the parent gas concentration, n_a the admixed gas concentration, and the $\bar{v}$'s are the appropriate average velocities of relative motion between the colliding particles. If the last term of Eq. (4) is small compared to the sum of the others, the differential equation is approximately linear in M and may be solved by the usual separation techniques. The fundamental solution of Eq. (4) is

$$M \simeq M_0 \exp(-t/T_m), \tag{8}$$

where M_0 is the initial metastable concentration and contains the spatial dependence,

$$1/T_m = (D_m/\Lambda^2) + \nu_d + \nu_i, \tag{9}$$

and Λ is the characteristic diffusion length of the container.[12]

In low pressure noble gas afterglows, electrons and ions are lost chiefly by ambipolar diffusion to the walls of the container.[13] The production of electrons and ions during the afterglow is the result either of metastable-metastable collisions [Eq. (1)] or of metastable-admixed atom collisions [Eq. (3)]. In order to obtain data which are interpretable in simple fashion, the experiments are arranged so that either the reaction of Eq. (1) or of Eq. (3) dominates. As a result, the electron density during the afterglow obeys one of the two following equations:

$$\partial n/\partial t = D_a \nabla^2 n + \alpha_I M^2, \quad \text{metastable-metastable;} \tag{10a}$$

$$\partial n/\partial t = D_a' \nabla^2 n + \nu_i M, \quad \text{metastable-admixed;} \tag{10b}$$

where n is the electron (or positive ion) density, D_a is the ambipolar diffusion coefficient of the ions produced by metastable-metastable collisions, and D_a' is the ambipolar diffusion coefficient of the ionized admixed atoms.

If we substitute the time dependence for M given by Eq. (8) into Eqs. (10a) and (10b), we find for the lowest mode solutions

$$n = A \exp(-t/T_D) - B \exp(-2/T_m) \tag{11a}$$

and

$$n = A' \exp(-t/T_D') - B' \exp(-t/T_m), \tag{11b}$$

where

$$T_D = \Lambda^2/D_a, \quad B = \alpha_I M_0^2/(2/T_m - 1/T_D),$$

and

$$A = n(t=0) + B; \quad B' = \nu_i M_0/(1/T_m - 1/T_D'),$$

and

$$A' = n(t=0) + B'.$$

Equation (11a) is an approximate solution for the electron density since the spatial distribution of the ionization produced by the metastable-metastable reaction does not correspond exactly to the lowest mode of electron density distribution. However, analysis shows that the higher order terms will affect our measurements of the metastable time constant by less than five percent.[14]

Equations (11a) and (11b) indicate that a study of the build-up and decay of electron density following a pulsed discharge affords a direct measurement of the metastable ionizing rates and yields values of the metastable lifetimes. From studies of the variation of T_m, B, and B' as a function of parent gas density, admixed gas density, and metastable atom concentration, we can determine diffusion coefficients, de-excitation cross sections, ionizing cross sections, and initial metastable atom densities.

Before discussing the experimental measurements, it might be well to dispose of the question of why the metastable ionization, which contributes only a fraction of the total ionization *during* the discharge, results in an initial *increase* in electron density after the ionizing

[11] A third type of de-excitation collision involves formation of an excited molecule at the collision of the metastable atom and two normal atoms (see reference 2). This process was not of importance under the conditions of the present experiment.

[12] For a cylinder of radius R and height H,

$$\Lambda = [(\pi/H)^2 + (2.4/R)^2]^{-\frac{1}{2}}.$$

[13] Ambipolar diffusion, which is the simultaneous diffusion of electrons and ions in the presence of their space charge field, is discussed in M. A. Biondi and S. C. Brown, Phys. Rev. **75**, 1700 (1949).

[14] T. Holstein, private communication.

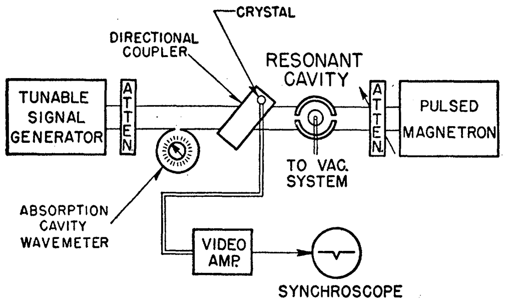

FIG. 1. Simplified block diagram of apparatus.

electric field is removed. During the discharge period, a stationary state is attained in which ionization by electron impact (~90 percent of the total ionization) and by metastable atoms balances the diffusion loss of electrons and ions.[15] During the afterglow, when the primary ionization (electron impact) ceases, the metastable atoms become the only source of ionization. If there were no change in the diffusion loss rate, one would expect the electron density to decrease monotonically during the afterglow. However, the electrons, which had an average energy of ~3 ev during the discharge, quickly lose their initial energy by recoil impacts with normal atoms and come to thermal equilibrium with the gas during the first 100 microseconds of the afterglow. This decrease in energy of the electrons causes a hundredfold decrease in the diffusion loss rate. Since the ionization rate has decreased only by a factor of ten, ionization by metastable atoms initially outweighs diffusion loss, and hence the electron density increases.

The mathematical formulation of this argument is contained in Eqs. (11a) and (11b). If the diffusion frequency, $1/T_D$, during the afterglow remained at the discharge value, then $1/T_D > 2/T_m$ and $1/T_D' > 1/T_m$, respectively. As a result, B and B' would be negative quantities; Eqs. (11a) and (11b) then indicate a monotonic decrease in electron density. Actually, the rapid "cooling" of the electrons by recoil collisions quickly reduces the diffusion rate $1/T_D$ to the point where it is less than the metastable ionization rate with the result that B and B' are positive, and an increase in electron density is indicated.

IV. EXPERIMENTAL METHOD

Microwave techniques are used to study the variation in electron density following a pulsed discharge. A detailed description of the method is given in an earlier paper.[16] The apparatus is shown in a simplified block diagram in Fig. 1. The gas to be studied is contained in a cylindrical quartz bottle (0.88-in. radius, 1.5-in. height) which is surrounded by a cavity resonant at roughly 3000 mc/sec. The gas is ionized by a pulse of power from the magnetron lasting ~300 μsec. Following the magnetron pulse, the variation in the electron density is determined by measuring the changing resonant frequency of the cavity. Under suitable experimental conditions, the change in resonant frequency is linearly proportional to the average electron density; the proportionality constant is calculable if the electric field distribution and the electron density distribution within the cavity are known. In this way, absolute values of the average electron density are obtained from measured frequency shifts.

In order to determine at what time during the afterglow the cavity has a particular resonant frequency, we observe the reflection of a *CW* signal of that frequency by the cavity. At the instant when the cavity's changing resonant frequency is equal to the signal frequency, the cavity absorbs the incident energy with the result that the reflected signal becomes a minimum. The signal's frequency is determined by the absorption cavity wave meter, and its reflection from the cavity is observed with the directional coupler, crystal, and video amplifier. The reflected signal is displayed on a synchroscope with a time-calibrated sweep. By noting the time at which minimum reflection occurs (resonance indication) for a number of different signal frequencies, we determine the resonant frequency of the cavity as a function of time, and from this the electron density during the afterglow.

To assure meaningful results, special care was used with regard to the purity of the gas samples studied. The vacuum system used in gas handling was of glass and metal throughout.[17] Metal valves[18] capable of high temperature bakeout were used for gas metering. The complete system (excluding the pumps) was baked at 420°C for 12 hours or more before each run. The residual pressure attained was $\sim 10^{-9}$ mm Hg, and the rate of rise of pressure in the system when isolated from the pumps and the pumping action of the ion gauge was $\sim 10^{-9}$ mm Hg/min. The gas samples used were either flasks of reagent grade gas from Air Reduction Company[19] or special flasks of very pure helium prepared by superleak techniques.[20]

V. MEASUREMENTS

An example of experimental measurements is given in Fig. 2 for the case of metastable-metastable ionization in low pressure helium and neon afterglows. In order to test the hypothesis that this initial increase in electron density is the result of ionization by metastable atoms, an experiment was performed in which the metastable atom concentration was reduced and the corresponding effect on the electron density noted. It

[15] See Sec. VI.

[16] M. A. Biondi, Rev. Sci. Instr. **22**, 500 (1951).

[17] The vacuum system is of a standard design evolved by the Atomic Physics Group at Westinghouse. The general features of such systems are described in an article by D. Alpert, Rev. Sci. Instr. (to be published).

[18] D. Alpert, Rev. Sci. Instr. **22**, 536 (1951).

[19] In most cases the significant impurities were present to $\lesssim 1:10^6$.

[20] M. A. Biondi, Rev. Sci. Instr. **22**, 535 (1951).

was found that irradiation of the helium afterglow with the 20,580A line (corresponding to the singlet $2P-2S$ transition) diminished the initial rise of electron density. Absorption of this line by a singlet metastable helium atom causes transfer to the $2P$ radiating state which may then return to ground state by emission of the resonance line. In this way, it was shown that reduction of the singlet metastable density resulted in decreased ionization during the afterglow. Irradiation by the 10,830A (triplet $2P-2S$) line, which can be absorbed by the triplet metastable atom, produced no effect on the electron density rise. Since an atom raised to the $2P$ triplet state can only radiate to the $2S$ triplet metastable state, irradiation with this line did not affect the metastable concentration and, hence, could not affect the electron density curves.

The data in Fig. 2 are analyzed in the following manner: The final slope of the measured density curve, n, is extrapolated back to early times. The difference between this extrapolated curve and the measured curve corresponds to the second term of Eq. (11a). This difference curve is shown plotted as Δn in Fig. 2. The slope of this curve is equal to $T_m/2$. Measurements of T_m were made in pure helium and in pure neon as a function of gas density. According to Eq. (9), in the absence of an ionizable admixed atom the decay constant, $1/T_m$, depends upon a diffusion term which is inversely proportional to the gas pressure and a de-excitation term which is linearly proportional to pressure. If Eq. (9) is multiplied by pressure, the first term on the right becomes constant and the second term proportional to pressure squared, that is,

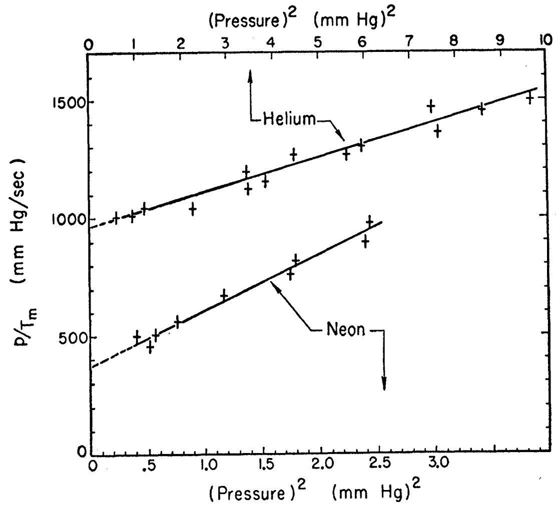

FIG. 3. Variation of metastable decay rate with gas pressure.

$$p/T_m = \frac{D_m p}{\Lambda^2} + Cp^2. \qquad (12)$$

Plots of p/T_m vs p^2 for helium and for neon are shown in Fig. 3.[21] From the intercept we calculate the metastable diffusion coefficient, while the slope yields the de-excitation rate. The results of these measurements are summarized in the first two columns of Table I.

In order to study the ionization of admixed atoms, small amounts of argon were added to helium and to neon, and in a third experiment mercury was added to helium. In these experiments, conditions were arranged so that the ionization of admixed atoms greatly outweighed ionization by metastable-metastable collisions. For this case Eq. (10b) describes the production and loss of electrons, and hence the electron density follows the law given in Eq. (11b). In the He-A and Ne-A experiments, 0.115 percent A was added to helium and to neon. The He-A studies were carried out over the range 1.6 to 3.2 mm Hg of helium; the Ne-A studies between 1.4 and 4.7 mm Hg of neon.

In the He-Hg experiments 1.8 mm of helium were added to a sealed-off bottle containing a drop of mercury. The vapor pressure of the mercury was then controlled by varying the temperature of a cold tip on

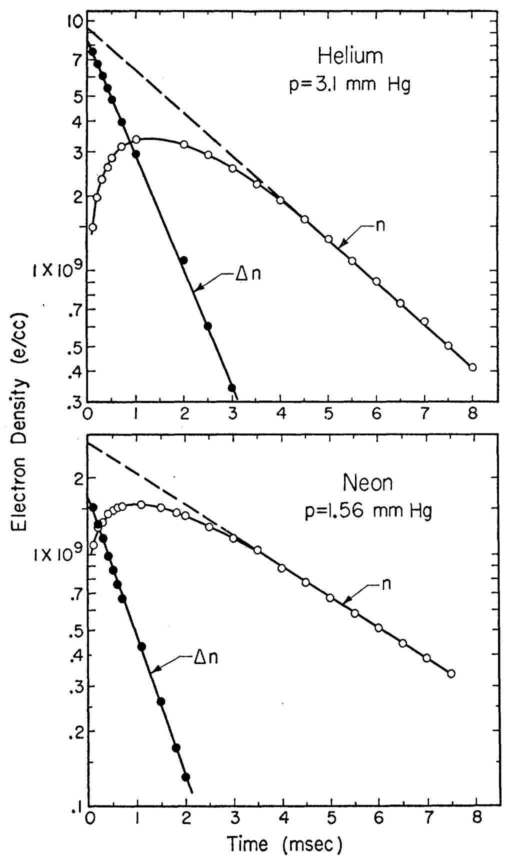

FIG. 2. Measured electron density, n, and derived difference density, Δn, in helium and neon afterglows.

[21] The maximum gas pressure used in these studies is limited by the increasing importance of conversion of the atomic ions to molecular ions which then recombine with electrons. In a region in which recombination loss is comparable to diffusion loss, Eqs. (10) and (11) no longer apply and analysis of the problem becomes extremely difficult.

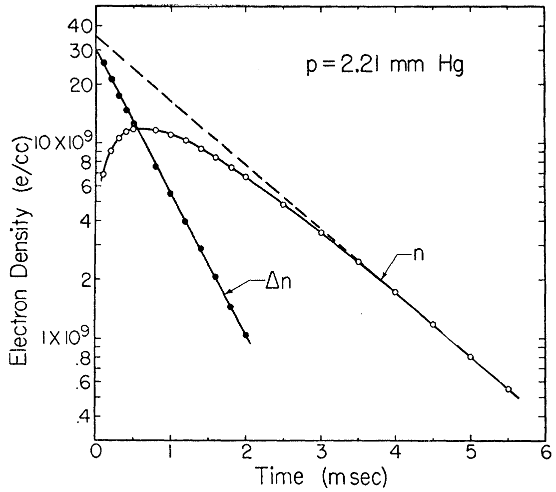

FIG. 4. Measured electron density, n, and derived difference density, Δn, in the afterglow of helium+0.115 percent argon.

the bottle. The He-Hg studies involved variation of the Hg vapor pressure from 2×10^{-7} to 1×10^{-5} mm Hg.

Typical data obtained in studies of ionization of argon atoms by helium metastable atoms are shown in Fig. 4. Here the difference curve, Δn, corresponds to the second term of Eq. (11b) so that its slope gives us T_m. Measurements of T_m permit us to calculate ν_i from Eq. (9) since the other two terms, D_m/Λ^2 and ν_d, were determined in the studies on pure helium. We calculate the cross section for ionization of argon atoms, σ_i, from our values of ν_i by use of Eq. (6). The results of the measurements are shown in Fig. 5. Similar results were obtained for the Ne-A and He-Hg experiments.

VI. RESULTS

The results of various measurements are summarized in Table I. The cross sections σ_d and σ_i are believed to be accurate to ±10 percent, except for σ_i of mercury which involves an uncertainty of ±20 percent. In addition to these coefficients and cross sections, we are able to determine initial metastable concentrations from the intercepts of the difference density curves. According to Eqs. (11a) and (11b), the intercepts give values of B and B', respectively, which in turn involve the initial metastable concentrations, M_0. We have calculated values of M_0 for two typical runs. For the case of metastable-metastable ionization in pure helium, we find an initial concentration of 5×10^{10} metastables/cc at 2.5 mm Hg.[22] For the case of ionization of argon by helium, we find an initial density of 2.5×10^{10} metastables/cc at 2.2 mm Hg pressure. These values permit us to estimate the fraction of ionization during the microwave discharge which is supplied by metastable ionization reactions.

During the discharge, a stationary state is attained in which the production of electrons and ions is balanced by their diffusion loss to the walls. The diffusion rate is simply $\nu_D n$, where $\nu_D=1/T_D$ is the diffusion rate per electron[23] and n is the electron density during the discharge. This loss rate is equal to the total production rate. The production during the discharge due to metastable atoms is either $\alpha_I M_0^2$ or $\nu_i M_0$, depending on which ionizing reaction is dominant. The ratios $\alpha_I M_0^2/\nu_D n$ and $\nu_i M_0/\nu_D n$ then yield the fraction of ionization due to metastables for the two types of reaction.

It is found that during the discharge in pure helium ~10 percent of the ionization is contributed by metastable-metastable collisions while in helium containing 0.1 percent argon ~25 percent of the ionization is the result of metastable atoms. These appreciable percentages emphasize the importance of this indirect ionization. Since conditions in the microwave discharge are very similar to those found in the positive column of dc or low frequency ac discharges, it is clear that proper account should be taken of metastable ionization in calculations on these types of discharges.

We have compared our measured diffusion, de-excitation, and ionization cross sections, as summarized in Table I, with measurements made by Molnar and Phelps[2] using modern optical absorption techniques. The diffusion coefficients for metastable atoms in helium and in neon agree within experimental error with the optical absorption measurements. Molnar and Phelps find no de-excitation for helium which follows the law given in Eq. (12), in contrast to our results. It should be noted that their measurements apply to the triplet metastable of helium, while our irradiation experiments (see Sec. V) indicate that we are measuring, at least in part, ionization produced by the singlet metastable. In order to eliminate the possibility that our observed de-excitation resulted from a small impurity in the helium, special flasks of very pure helium

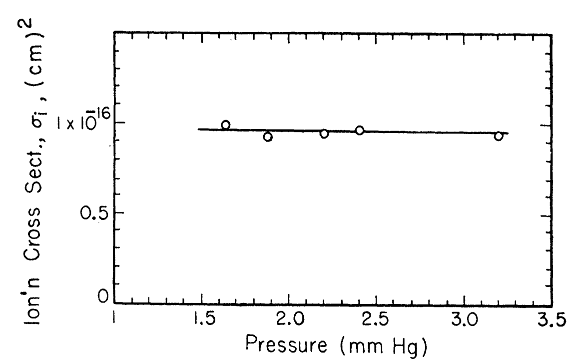

FIG. 5. Cross section for the ionization of argon atoms by helium metastables measured in helium containing 0.115 percent argon.

[22] For this estimate the value of the metastable-metastable ionizing cross section in helium was taken as 10^{-14} cm². The author is indebted to A. V. Phelps for making available this preliminary value from absorption experiments.

[23] Calculation of the ambipolar diffusion rate during the discharge follows the procedure given in A. von Engel and M. Steenbeck, *Electrische Gasentladungen* (J. Springer, Berlin, 1932), Vol. 1, p. 183 ff.

were prepared using superleak techniques.[20] This helium was conservatively estimated to contain less than one part in 10^9 of impurity. The results given in Figs. 2 and 3 are for this special helium. From these measurements, we conclude that the de-excitation collisions were not the result of impurities.

De-excitation of a helium singlet metastable atom will result if it is sufficiently perturbed on collision with a normal atom to cause radiation to the ground state. A qualitative estimate for the probability of this process[24] indicates that it could account for our observed de-excitation rate. Quantitative calculations are not possible since they require detailed knowledge of the potential energy curves of the various excited states during the collision.

The de-excitation cross section for neon is in order of magnitude agreement with the optical absorption results. Here the de-excitation of the metastables is thought to involve the actual transfer of the metastable to a nearby radiating state on collision with normal atoms. In the absence of any quantitative theory for the probability of this process,[10] we can only conclude that our measured cross section is reasonable in magnitude.

The cross sections for ionization of argon by helium and neon metastables are in reasonable agreement with the results of Molnar and Phelps. The Ne-A result modifies the previous value obtained by Penning's group at Eindhoven.[4] Our value for the ionizing cross section is an order of magnitude smaller than their value. In view of the greater certainty of the present method and of the modern optical absorption studies,[2] we feel that the Eindhoven value is in error.[25]

The cross section for ionization of mercury by helium metastables is two orders of magnitude larger than for argon. MacDonald and Brown[26] have computed the breakdown potential of helium gas containing a small amount of mercury. An underlying assumption of their theory is that each helium atom which is excited to a metastable state ionizes a mercury atom, so that the first excitation potential of helium is the effective ionization potential for the He-Hg mixture. For this assumption to be valid, it is necessary that the He-Hg ionizing cross section be rather large. Our measured value of 10^{-14} cm^2 may be sufficiently large to justify their assumption.

TABLE I. Measured values for helium and neon metastable atoms.

Parent gas	$D_m p$(cm^2/sec)-(mm Hg)	σ_d(cm^2)	σ_i(cm^2)
Helium	520±20	9.6×10^{-21}	Argon 9.7×10^{-17} Mercury 1.4×10^{-14}
Neon	200±20	8.9×10^{-20}	Argon 2.6×10^{-16}

VII. DISCUSSION

The present measurements of ionization occurring in the afterglow of a microwave discharge confirm the hypothesis of Schade and Büttner[6] that collisions between pairs of metastable atoms produce significant ionization. The measurements on gas mixtures have extended the work of Penning's group[4] and have yielded more precise measurements of the ionizing cross sections. In addition, these studies have yielded values of the metastable diffusion and de-excitation cross sections which agree reasonably well with the results of modern absorption studies, indicating the value of microwave afterglow studies for measuring metastable lifetimes.

The author wishes to thank the members of the Atomic Physics group at Westinghouse for interesting discussions of this work. The author is particularly indebted to T. Holstein, who pointed out the metastable-metastable hypothesis and its consequences and contributed many valuable suggestions.

[24] One estimates the time of collision during which the metastable 2^1S_0 state is sufficiently perturbed by the colliding atom to cause a strong admixture of 2^1P_1 state. The ratio of this time to the natural radiative lifetime of the 2^1P_1 state gives the probability of de-excitation by collision-induced radiation.

[25] G. Schut and J. A. Smit, Physica **10**, 440 (1943), obtain a preliminary value, $\sigma_i=6.7\times10^{-16}$ cm^2 for Ne-A, in order of magnitude agreement with our value.

[26] A. D. MacDonald and S. C. Brown, Phys. Rev. **75**, 411 (1949).