probable enough to produce an appreciable concentration of N atoms by the action of sunlight.

To test for the occurrence of N atoms we must answer two questions. (1) Is the higher value of the energy of dissociation of N_2 required to explain the spectrum of the airglow, in particular the occurrence of the Vegard-Kaplan bands? Here one may question the rather uncertain observation which seems to show these bands with vibrational quantum numbers as high as $v'=9$. If this observation is correct the excitation energy would be sufficient to excite as well the first positive group ($v'=0$ or 1) which in laboratory experiments is the most prominent feature of the nitrogen spectrum but is absent in the airglow. (2) Do the observations indicate the absence of N atoms? That the spectrum of the aurora exhibits *molecular* nitrogen with predominant intensity does not contradict the occurrence of a large concentration of *atomic* nitrogen. This is illustrated by the low pressure discharge which, although emitting almost exclusively the molecular spectrum, produces a large concentration of atomic nitrogen which is evident as "active" nitrogen. At low excitation the spectrum of N atoms consists only of two forbidden lines which do appear in some low pressure discharges and the aurora but are absent from the airglow. These various observations are compatible with the partial dissociation of nitrogen in the airglow if we adopt the following plausible assumptions: In the low pressure discharge the N lines are observed only in very pure nitrogen, indicating that impurities, but not nitrogen atoms or molecules, deactivate the metastable N atoms. In the airglow the absence of the N lines may be due to deactivation by oxygen. In the aurora, where the N lines sometimes appear, it is possible that they are emitted at high altitudes where collisions are very rare. Therefore, the absence of N lines in the airglow and their occasional presence in the aurora leads to the speculation that in any case N atoms are present and excited to metastable levels but are able to radiate only if not quenched by oxygen. Presumably the emission of the forbidden lines in the aurora takes place in altitudes much higher than that of the airglow. This prediction ought to be accessible to direct observation.

The author wishes to express his appreciation to Mr. D. G. Bills for his cooperation.

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Processes Involving Ions and Metastable Atoms in Mercury Afterglows

Manfred A. Biondi
Westinghouse Research Laboratories, East Pittsburgh, Pennsylvania

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Atomic collision processes occurring in mercury vapor are determined from microwave measurements of the electron density during the afterglow. The electrons are brought into thermal equilibrium with the gas by adding helium to the mercury vapor to act as a "recoil gas." Measurements of the ambipolar diffusion coefficient, D_a, of Hg^+ ions and electrons in helium yield the value $D_an=2.6\times10^{19}$ (cm^2/sec)(atoms/cc) at 290°K. The corresponding value for Hg^+ ions in mercury is $D_an=3.6\times10^{17}$ at 350°K. Conversion of the atomic mercury ions to molecular ions according to the reaction $Hg^++Hg+He\rightarrow Hg_2{}^++He$ occurs at the rate of 140 $(p_{Hg}\cdot p_{He})$ sec^{-1}. The measured recombination coefficient of $Hg_2{}^+$ ions with electrons is $\alpha=5.5\times10^{-7}$ cc/sec at 400°K. Studies of the ionization produced by the collisions of pairs of mercury metastable atoms yield the values $D_mn=1.5\times10^{18}$ (cm^2/sec)(atoms/cc) for the diffusion coefficient and $\sigma_d=8\times10^{-17}$ cm^2 for the de-excitation cross section of $^3P_2$ metastables at 350°K.

In recent years, atomic collision processes occurring in ionized gases have been studied by the use of microwave techniques. Measurements of the variation of the electron density in the afterglow of a pulsed discharge have yielded information concerning processes involving electrons, ions, and excited atoms. Under conditions in which the electrons have been in thermal equilibrium with the gas, it has been possible to obtain quantitative measurements for the probabilities of the various collision processes.

Studies of electron removal in mercury afterglows have been carried out by Mierdel[1] and by Dandurand and Holt,[2] using Langmuir probe and microwave techniques, respectively. In these investigations the electrons were not in thermal equilibrium with the gas. As a result, only qualitative remarks could be made concerning the processes occurring in mercury. In the present experiment the electrons are brought into thermal equilibrium with the gas by adding helium to the mercury vapor to act as a "recoil gas." Quantitative values for the various collision processes are then obtained from the afterglow measurements.

I. EXPERIMENTAL METHOD

Microwave techniques are used to measure the electron density during the afterglow following a pulsed discharge in mercury. Detailed descriptions of the

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[1] G. Mierdel, Z. Physik **121**, 574 (1943).

[2] P. Dandurand and R. Holt, Phys. Rev. **82**, 868 (1951).

method are contained in the literature.[3] The gas to be studied is contained in a cylindrical quartz bottle inside a cavity resonant at approximately 3000 Mc/sec. The gas is ionized by application of a pulse of microwave power from a magnetron. The free electrons in the ionized gas cause a change in the resonant frequency of the cavity. Under the experimental conditions, the change of the cavity's resonant frequency is directly proportional to the average electron density in the cavity. A low-level probing signal is used to measure the resonant frequency of the cavity as a function of time. From these measurements, we calculate the electron density during the afterglow.

The resonant cavity takes the form of an oven to permit variation of the vapor density and temperature of the mercury (see Fig. 1). The mercury-helium sample under study is enclosed in a sealed-off quartz bottle which had been evacuated to a pressure of 10^{-8} mm on an ultra-high vacuum system[4] exhibiting a rate of rise of impurity pressure of less than 10^{-9} mm Hg/min. The temperature and the vapor density of the mercury were controlled independently by the use of two separate ovens. The upper oven, which formed the microwave cavity, controlled the vapor temperature. The lower oven was used to control the vapor density. Thermocouples were used to measure the temperature at various points. Unless otherwise noted, the temperature of the upper oven was approximately one degree above the temperature of the lower oven.

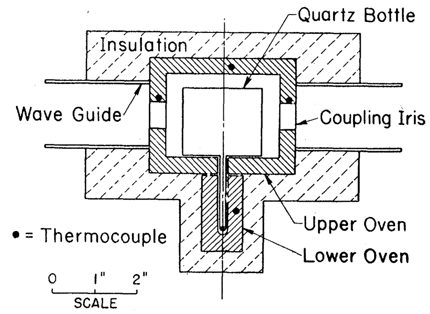

FIG. 1. Microwave cavity-oven. The upper oven, which forms the microwave resonant cavity, controls the vapor temperature while the lower oven controls the vapor density. The thermocouples are used to measure the temperatures at various points.

II. PRODUCTION OF THERMAL ELECTRONS IN MERCURY AFTERGLOWS

Quantitative measurements of the collision processes occurring in a gas are readily obtained from afterglow studies in which the electrons are in thermal equilibrium with the gas. During the discharge, the electrons have an average energy of the order of 1 ev. When the ionizing field is removed, the electrons lose this energy chiefly by elastic recoil collisions with the gas atoms and finally come into thermal equilibrium with the gas. We may define an energy relaxation time, T_R, of the electrons by

$$T_R=(M/2m)T_c, \tag{1}$$

where M and m are the masses of the gas atom and electron, respectively, and T_c is the mean time between elastic collisions. If this collision time is not a function of the electron energy, T_R is the time required for the electron energy to diminish by a factor $1/e$.

Using the data of Adler and Margenau[5] to compute the elastic collision time in mercury, we find that for electrons whose energy is a few tenths of an electron-volt this relaxation time is approximately $(10^{-4}/p)$ sec, where p is expressed in mm Hg. Since our measuring intervals are of the order of milliseconds, measurements at pressures less than 1 mm are complicated by the fact that the electrons are not in thermal equilibrium with the gas during the measuring interval. In the present experiment, this difficulty has been avoided by adding helium to the mercury vapor to act as a "recoil gas." Since helium atoms are much lighter than mercury atoms, they are more effective in removing the electrons' excess energy in elastic recoil collisions [see Eq. (1)]. In addition, the excitation potentials of helium are sufficiently large to assure that the helium atoms are not excited in most of the experiments. As a result, the helium does not interfere with studies of the behavior of ionized mercury atoms.

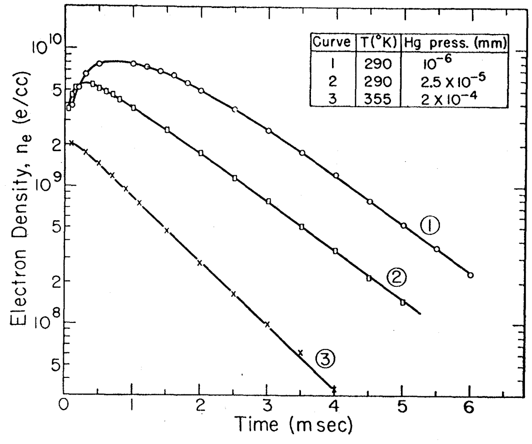

FIG. 2. Production and loss of mercury ions in helium. These measurements were made at a constant helium density of 5.8×10^{16} atoms/cc.

Helium at a density of 5.8×10^{16} atoms/cc (1.8 mm at 300°K) is added to a sealed-off quartz bottle containing a drop of mercury; consequently, the energy relaxation time is reduced to less than 10 μsec.[6] The electrons now come into thermal equilibrium with the gas during the first 100 μsec of the afterglow and

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

[4] The vacuum system is similar to those described by D. Alpert, J. Appl. Phys. (to be published). Chemically pure mercury (99.98 percent) was doubly distilled into the quartz bottle, and Airco reagent grade helium was added before seal-off from the system.

[5] F. P. Adler and H. Margenau, Phys. Rev. **79**, 970 (1950).

[6] The elastic collision probability is obtained from R. B. Brode, Revs. Modern Phys. **5**, 257 (1933).

remain in thermal equilibrium during the remainder of the measuring interval.

III. PRODUCTION AND DIFFUSION OF MERCURY IONS IN HELIUM

Studies of the mercury afterglows were carried out over a very wide range of mercury vapor densities. Initially, the lower oven of Fig. 1 was replaced by a low temperature bath. At a bath temperature of 77°K, the mercury vapor pressure was reduced essentially to zero. The electron density variation during the afterglow was then characteristic of the behavior previously observed for pure helium at 1.8 mm Hg.[7,8] As the bath temperature was increased to the point where the vapor pressure of mercury lay in the range $10^{-6}-2\times10^{-4}$ mm Hg, the data indicated the production of electrons during the afterglow by the Penning reaction and the ambipolar diffusion loss of mercury ions and electrons. The Penning ionizing reaction for helium containing mercury is

$$\mathrm{He}^*+\mathrm{Hg}\rightarrow\mathrm{Hg}^++e+\mathrm{He}, \tag{2}$$

where * indicates an atom raised to a metastable state. Examples of experimental data for three vapor pressures and two vapor temperatures are shown in Fig. 2. It has been shown[7] that when electrons are produced by metastable atoms according to reaction (2) and lost by ambipolar diffusion, the electron density, n_e, obeys the following equation:

$$n_e=A'\exp(-t/\mathrm{T}_D)-B'\exp(-t/\mathrm{T}_m), \tag{3}$$

where T_D is the decay time due to ambipolar diffusion of mercury ions and electrons, T_m is the helium metastable decay time, and A' and B' are constants. The data of Fig. 2 obey Eq. (3). The behavior of the helium metastables is discussed in reference 7. The final slope of the curves of Fig. 2 yields the ambipolar diffusion time constant, T_D, which is related to the ambipolar diffusion coefficient D_a by[8]

$$D_a=\Lambda^2/\mathrm{T}_D, \tag{4}$$

where Λ is the characteristic diffusion length of the container.[9] It is found that $D_a=440$ cm²/sec for mercury ions diffusing through helium at a density $n=5.8\times10^{16}$ atoms/cc and a temperature of 290°K.

The ambipolar diffusion coefficient is related to the diffusion coefficients and mobilities of the ions and electrons by[10]

$$D_a=\frac{D_+\mu_e+D_e\mu_+}{\mu_e+\mu_+}\simeq D_+\left(1+\frac{T_e}{T_+}\right), \tag{5}$$

where D, μ, and T are the diffusion coefficient, mobility, and temperature, respectively, of each particle, and the subscripts $_+$ and $_e$ refer to ions and electrons. Thus measurements of the ambipolar diffusion of *electrons* yield values of the *ionic* diffusion coefficient when the ionic and electron temperatures are known. In the present experiment in which thermal equilibrium is attained, $T_e=T_+=T_{\mathrm{gas}}$.

The ionic diffusion coefficient is given by[11]

$$D_+=\langle lv_r/3\rangle_{\mathrm{Av}}=\langle v_r/3n\sigma_D\rangle_{\mathrm{Av}}, \tag{6}$$

where l is the mean free path, v_r the random velocity, σ_D the diffusion cross section of the ions, and n is the density of the gas in which the ions diffuse. Curves 1 and 2 of Fig. 2, taken at the same temperature but at different mercury atom concentrations, exhibit the same diffusion time constant, indicating that the diffusion is controlled by collisions of mercury ions with *helium* atoms. The diffusion cross section of mercury ions in helium is expected to vary inversely with the velocity of the colliding particles (polarization interaction). As a result, Eq. (6) predicts that the ionic diffusion coefficient varies directly with the ion temperature at constant gas density. The ratio of the diffusion coefficients obtained from curve 3 ($T=355$°K) and from curves 1 and 2 ($T=290$°K) is 1.30, while the temperature ratio is 1.23, agreeing within experimental error with the predicted behavior. The diffusion coefficient obtained from these measurements may be compared with measurements of alkali ion mobilities in helium by use of the following relation:[11]

$$D_+=(kT_+/e)\mu_+. \tag{7}$$

Our measurements yield the value $\mu_+=19.9$ cm²/volt-sec for the mobility of mercury ions moving in helium at 760 mm Hg pressure and 291°K. This value agrees with an extrapolation of the mobility *vs* mass curve observed by Munson and Tyndall[12] for the alkali ions, confirming our interpretation that mercury ions are formed and diffuse in helium.

IV. DIFFUSION AND CONVERSION OF MERCURY IONS IN MERCURY

As the vapor density of the mercury is increased above 10^{13} atoms/cc, collisions of mercury ions with mercury atoms modify the ambipolar diffusion. At vapor densities in excess of 6×10^{14} atoms/cc, the diffusion of the ions is controlled by collisions with mercury atoms rather than with helium atoms. Over the range of densities 6×10^{14} to 3.4×10^{15} atoms/cc, it is found that the electron density decay time T increases with the mercury vapor density according to the relation,

$$\mathrm{T}=(1.5\times10^{-18}n)\ \mathrm{sec}, \tag{8}$$

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[7] M. A. Biondi, Phys. Rev. **88**, 660 (1952).

[8] M. A. Biondi and S. C. Brown, Phys. Rev. **75**, 1700 (1949).

[9] In the present experiment, the diffusion takes place in a cylinder of radius $R=2.22$ cm and height $H=3.82$ cm, for which $\Lambda=0.735$ cm.

[10] A. von Engel and M. Steenbeck, *Electrische Gasenltadungen* (J. Springer, Berlin, 1932), Vol. I, p. 199. The concept of electron and ion "temperature" applies only to cases in which the particles have Maxwellian velocity distribution.

[11] E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1938), p. 194 ff.

[12] R. J. Munson and A. M. Tyndall, Proc. Roy. Soc. (London) **A172**, 28 (1939).

where n is expressed in atoms/cc. This variation of the decay time with mercury vapor density is characteristic of the diffusion of mercury ions in mercury and leads to the value $D_a n = 3.6 \times 10^{17}$ (cm^2/sec)(atoms/cc) at a temperature of 350°K.

The chief interaction between a mercury ion and a mercury atom results from charge transfer. This interaction leads to a diffusion cross section which is practically independent of the ion's energy.[13] As a result [see Eq. (6)], the diffusion coefficient is expected to vary as the square root of the ionic temperature. This temperature correction was applied to the data to obtain Eq. (8). The measured ambipolar diffusion coefficient is in good agreement with the value $D_a n = 3.8 \times 10^{17}$ obtained from theory.[14]

As the vapor density is increased further, the measured decay time deviates from the diffusion law given by Eq. (8). It is found experimentally that the electron density decay time now obeys the relation

$$1/\mathrm{T} = A/n + Cn, \tag{9}$$

where A and C are constants. The first term represents diffusion loss and the second term a process whose rate is directly proportional to the mercury concentration. If Eq. (9) is multiplied by n, the first term on the right becomes invariant and the second term proportional to n^2. The experimentally measured values are illustrated in Fig. 3. The intercept of the curve is $(n/\mathrm{T})_0 = D_a n/\Lambda^2$. The slope of the curve of Fig. 3 gives us the values of C in Eq. (9).

There are two possible interpretations of the volume loss term, C. If the electrons are lost by attachment to mercury atoms to form negative ions, we interpret C as the attachment coefficient, which is related to the attachment cross section, σ_a, by

$$C = \sigma_a \bar{v}, \tag{10}$$

where $\bar{v}$ is the mean relative speed of the electrons. The measured slope then yields a value $\sigma_a = 7 \times 10^{-22}$ cm^2, which is the order of a radiative attachment cross section. Preliminary calculations of the effect of negative ion formation on the ambipolar diffusion loss of electrons indicate that the interpretation of C as the attachment coefficient applies only if the ratio of the negative ion to electron concentration remains small. Thus it appears that the assumption of electron attachment is open to question.

Alternatively, the increased rate of electron loss may result from the conversion of atomic mercury ions to molecular ions according to the reaction

$$\mathrm{Hg}^+ + \mathrm{Hg} + \mathrm{He} \rightarrow \mathrm{Hg}_2^+ + \mathrm{He}. \tag{11}$$

Unfortunately, experiments in sealed-off quartz bottles did not permit us to vary both the mercury and the helium concentrations in order to verify this reaction. Investigations of a similar reaction involving conversion of A^+ to A_2^+ in the presence of He or Ne are in progress. In these experiments, it is relatively simple to vary both the A and He or Ne concentrations. If the reaction (11) leads to the increased electron loss, the second term on the right of Eq. (9) is simply the conversion frequency which is found to be

$$\nu_{\mathrm{conv}} = 1.7 \times 10^{-31} (n_{\mathrm{Hg}} \cdot n_{\mathrm{He}}) = 140 (p_{\mathrm{Hg}} \cdot p_{\mathrm{He}})\ \mathrm{sec}^{-1}, \tag{12}$$

where n is expressed in atoms/cc and p in mm Hg.

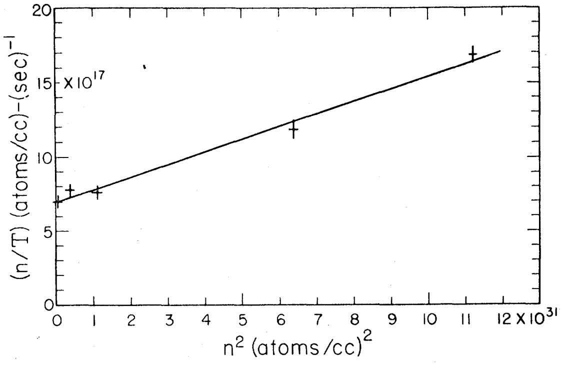

FIG. 3. Variation of electron density decay constant with mercury vapor density.

The explanation of why the conversion of atomic ions to molecular ions results in an increased rate of loss of electrons is as follows. At low pressures, the chief electron and ion removal process is ambipolar diffusion. It is expected[15] that the atomic ions diffuse more slowly than the molecular ions. It has been shown[16] that if atomic ions are converted to molecular ions at a rate which is smaller than the molecular ion diffusion rate, the rate of loss of electrons will be simply the combined rates of the ambipolar diffusion and conversion of atomic ions. At higher pressures recombination between molecular ions and electrons becomes important, since the diffusion decreases with increasing pressure. In this case, the electron density decay will still be determined by the combined atomic ion diffusion and conversion rates provided that the electron recombination rate[17] exceeds the conversion rate and that the molecular ion concentration remains small, i.e.,

$$\alpha M \gg \nu_{\mathrm{conv}}, \tag{13}$$

and

$$M \ll A < n_e, \tag{14}$$

where α is the recombination coefficient, M the molecular ion concentration, and A the atomic ion concentration.

As the vapor density is increased further the curve of Fig. 3 deviates from linearity, exhibiting an increased slope at high vapor density. This additional loss may

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[13] T. Holstein, J. Phys. Chem. **56**, 832 (1952).

[14] T. Holstein and I. B. Bernstein (private communication) have recently calculated the diffusion cross section of mercury ions in mercury following the procedure outlined in reference 13.

[15] R. Meyerott, Phys. Rev. **70**, 671 (1946).

[16] A. V. Phelps and S. C. Brown, Phys. Rev. **86**, 102 (1952).

[17] See Eq. (18) of the next section.

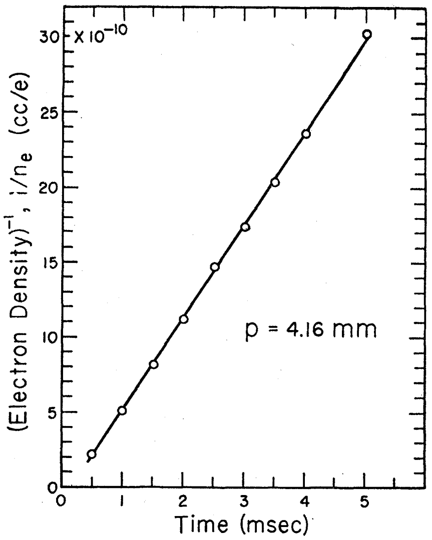

FIG. 4. Electron-ion recombination in mercury vapor.

result from the conversion reaction:

$$\mathrm{Hg}^+ + 2\mathrm{Hg} \rightarrow \mathrm{Hg}_2^+ + \mathrm{Hg}. \tag{15}$$

Our data indicate that reaction (15) leads to a conversion frequency of the order

$$\nu'_{\mathrm{conv}} \sim 10^{-31}(n_{\mathrm{Hg}})^2 \sim 100(p_{\mathrm{Hg}})^2 \ \mathrm{sec}^{-1}. \tag{16}$$

There are no theoretical calculations of the rates of reactions (11) and (15); however, the estimated values from the present experiment are the same order as are obtained experimentally for the conversion of He^+ to He_2^+.[16]

The experimental data presented so far do not clearly indicate whether the electron loss of Fig. 3 results from electron attachment to mercury atoms or from the conversion of atomic mercury ions to molecular ions. In the next section, it will be shown that interpretation in terms of conversion to molecular ions is consistent with the observation of a large recombination loss of electrons.

V. RECOMBINATION IN MERCURY

It has been shown previously[18] that the large recombination observed in microwave afterglows requires the presence of molecular ions. The process is evidently dissociative recombination, which in the case of mercury proceeds according to the reaction

$$\mathrm{Hg}_2^+ + e \rightarrow \mathrm{Hg}^* + \mathrm{Hg}, \tag{17}$$

where * indicates an excited atom. In the present experiment, it is observed that as the pressure is increased through the range, $p \sim 1$ mm Hg, the electron density decay curves show increasing evidence of recombination loss, indicating the formation of appreciable numbers of molecular ions.

The rate of removal of electrons and molecular ions by recombination is given by

$$dn_e/dt = -\alpha n_e M, \tag{18}$$

where α is the dissociative recombination coefficient. At sufficiently high pressures the ions in the afterglow are expected to be chiefly molecular in nature. If we require quasi neutrality in the afterglow plasma, then $n_e \simeq M$, and Eq. (18) becomes

$$dn_e/dt \simeq -\alpha n_e^2, \tag{19}$$

whose solution is

$$1/n_e = (1/n_e)_0 + \alpha t. \tag{20}$$

An example of the observed electron density variation when recombination is the dominant electron removal process is shown in Fig. 4. It should be noted that the determination of the absolute magnitude of the recombination coefficient requires knowledge of the absolute electron density. As a result of the finite collision frequency of electrons with mercury atoms, there is a correction needed in the formula relating the electron density to the change in resonant frequency of the cavity.[19] Using Adler and Margenau's[5] data for the elastic collision probability of electrons in mercury, we have corrected our electron density data for the finite collision frequency effect.

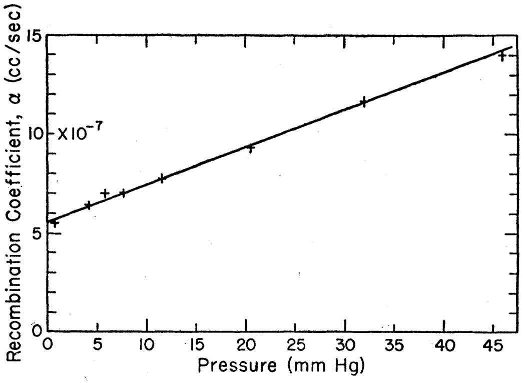

FIG. 5. Variation of the measured recombination coefficient with the vapor pressure of the mercury. The vapor temperature at each vapor pressure is approximately one degree higher than that of the liquid mercury so that the temperature varies from 407°K at 1.4 mm Hg to 505°K at 46 mm Hg.

The observed variation of the recombination coefficient with pressure is shown in Fig. 5. We interpret this pressure variation as follows: Dissociative recombination between electrons and ions of a given type is expected to be independent of gas pressure since the recombination is a two-body process involving only the ion and the electron. The observation of a pressure dependent recombination coefficient may therefore

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[18] M. A. Biondi and T. Holstein, Phys. Rev. **82**, 962 (1951); M. A. Biondi, Phys. Rev. **83**, 1078 (1951).

[19] The correction to be applied to Eq. (3), reference 3, has been calculated for various experimental arrangements by A. V. Phelps, doctoral thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1951 (unpublished).

indicate that two ions having different recombination coefficients are present during the afterglow and that their relative concentrations vary with the gas pressure. Loeb and Kunkel[20] have suggested such a scheme to account for pressure dependent recombination coefficients in hydrogen; however, their proposal encounters difficulty in explaining the observed form of the pressure dependence. In the present experiment, the linear dependence of α on pressure suggests an equilibrium reaction of the form

$$\mathrm{Hg_2^+ + 2Hg \rightleftharpoons Hg_3^+ + Hg}. \tag{21}$$

It is assumed that $\mathrm{Hg_3^+}$ has a weak binding energy (of the order of ten kT); therefore a quasi equilibrium exists between the concentrations of the two recombining ions. In this case the measured recombination coefficient has the form[20]

$$\alpha = (\alpha_2 + \alpha_3 Kn)/(1+Kn), \tag{22}$$

where α_2 and α_3 are the recombination coefficients of $\mathrm{Hg_2^+}$ and $\mathrm{Hg_3^+}$, respectively, K is the equilibrium constant of reaction (21), and n is the concentration of mercury atoms. This equation predicts a linear dependence of α on pressure provided that $Kn \ll 1$. At high pressures, $Kn \gg 1$, the curve is expected to approach the value α_3. Unfortunately, we were unable to obtain data at pressures in excess of 50 mm Hg. If measurements could be carried into the range where α_3 is determined, it would be possible to obtain the value of K and, hence, the binding energy of $\mathrm{Hg_3^+}$.

According to Eq. (22) the intercept of the curve of Fig. 5 yields the value of α_2. It is found that the dissociative recombination coefficient of $\mathrm{Hg_2^+}$ ions and thermal electrons ($T \simeq 400°\mathrm{K}$) is 5.5×10^{-7} cc/sec. This value is two orders of magnitude larger than that estimated by Dandurand and Holt[2] for recombination with "hot" electrons (T_e was estimated to be of the order of 2000°K). However, it is the same order of magnitude as has been found for thermal electrons recombining in noble gases such as Ne and A.[21]

VI. IONIZATION BY MERCURY METASTABLE ATOMS

The effect of ionization produced by metastable atoms in helium and in neon has previously been reported.[7] Corresponding studies of metastable atoms in mercury containing helium were not possible since it appeared that the mercury metastables were rapidly destroyed by the helium. However, measurements in pure mercury did show the effect of ionization by metastable atoms. The ionization resulted from collisions of pairs of metastable atoms:

$$\mathrm{Hg^* + Hg^* \rightarrow Hg^+ + \mathit{e} + Hg}. \tag{23}$$

This reaction is energetically possible if the sum of the metastable excitation energies exceeds the ionization potential. The ionization potential of mercury is 10.44 ev. The upper $^3P_2$ metastable level is 5.47 ev above the ground state, the lower $^3P_0$ metastable 4.67 ev above ground. If the ionizing reaction results in the formation of atomic ions,[22] it is clear that only the upper metastable states have sufficient energy for reaction (23).

If electrons are produced by metastable atoms according to Eq. (23) and are lost by ambipolar diffusion, the electron density obeys the equation[7]

$$n_e = A\exp(-t/\mathrm{T}_D) - B\exp(-2t/\mathrm{T}_m), \tag{24}$$

where T_D is the ambipolar diffusion decay time of mercury ions and electrons in mercury, T_m is the metastable decay time, and A and B are constants. We expect Eq. (24) to be applicable in cases where the ambipolar diffusion coefficient does not change with time. It is therefore necessary that the electron energy remain constant. In studies of pure mercury afterglows the electrons do not attain thermal equilibrium with the gas; however, there is evidence that their energy does not change appreciably during the measuring interval (see Sec. VII). As a result, the ambipolar diffusion coefficient is expected to be constant, and Eq. (24) should represent the experimental data accurately.

An example of the observed electron density variation during the afterglow in pure mercury is shown in Fig. 6.

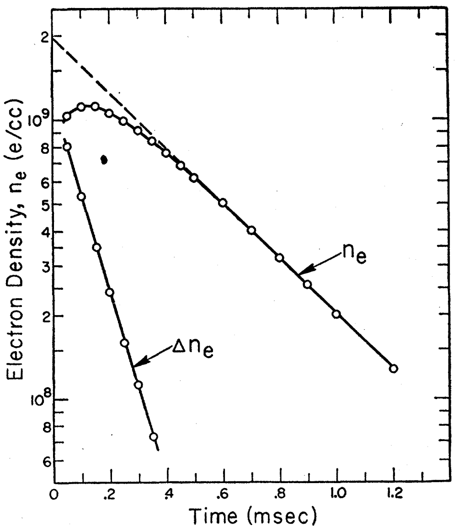

FIG. 6. Measured electron density, n_e, and derived difference density, Δn_e, during the afterglow in pure mercury. The mercury vapor density is 1.35×10^{15} atoms/cc, and the temperature, 350°K.

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[20] L. B. Loeb and W. B. Kunkel, Phys. Rev. **85**, 493 (1952).

[21] M. A. Biondi and S. C. Brown, Phys. Rev. **76**, 1697 (1949).

[22] In the corresponding studies of reaction (23) for helium and for neon, reference (7), it was possible to identify the ions formed as atomic ions by comparison of the measured ambipolar diffusion coefficients with known values. In the present experiment no such identification is possible, and the alternative reaction,

$$\mathrm{Hg^* + Hg^* \rightarrow Hg_2^+ + \mathit{e}},$$

must be considered as a possibility. This reaction will be energetically possible for the lower $^3P_0$ metastables as well as for the upper $^3P_2$ metastables if the binding energy of $\mathrm{Hg_2^+}$ is sufficiently large (>1.1 ev).

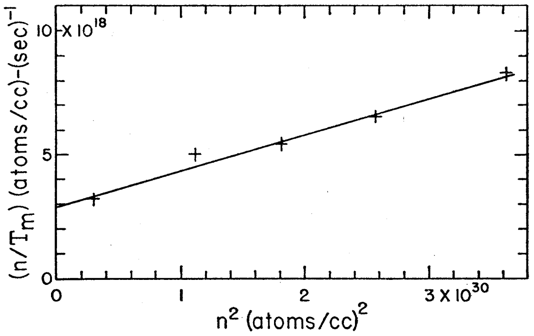

FIG. 7. Variation of the metastable decay rate with the mercury vapor density at $T \simeq 350°$K.

The final slope of the electron density curve gives us the diffusion time constant, T_D, while the slope of the difference density curve gives us $T_m/2$. The metastable mercury atoms are destroyed chiefly by diffusion to the walls and by collisions with normal mercury atoms. Therefore, the metastable time constant is given by

$$1/T_m = D_m/\Lambda^2 + n\sigma_d\bar{v}, \qquad (25)$$

where D_m is the metastable diffusion coefficient, σ_d the de-excitation cross section for collisions with normal atoms, and $\bar{v}$ is the mean relative speed of the colliding particles. Multiplication of Eq. (25) by n makes the first term on the right invariant and the second term proportional to n^2. The experimental values of n/T_m *vs* n^2 are shown plotted in Fig. 7. The intercept yields the value $D_m n = 1.5 \times 10^{18} \pm 10$ percent (cm^2/sec)-(atoms/cc) at $T = 350°$K. This value, which presumably applies to the $^3P_2$ metastable, may be compared with measured diffusion coefficients for the $^3P_0$ metastable. Coulliette[23] obtained a value $D_m n = 1.8 \times 10^{18}$, while McCoubrey[24] found the value 1.7×10^{18}.

The slope of the curve of Fig. 7 yields the de-excitation cross section, $\sigma_d = 8 \times 10^{-17} \pm 10$ percent cm^2. This cross section for the destruction of the upper metastable state is rather large; unfortunately, theoretical calculations of the cross section are not available for comparison.*

VII. AMBIPOLAR DIFFUSION IN PURE MERCURY

In the preceding section, it was pointed out that the final slope of the electron density curve of Fig. 6 gave the ambipolar diffusion time constant, T_D. Over the range of mercury vapor densities, $6 \times 10^{14} - 2 \times 10^{15}$ atoms/cc, the measured diffusion decay times yield a value $D_a n = 1.4 \times 10^{18} \pm 20$ percent (cm^2/sec)(atoms/cc) at 350°K. This value, obtained for pure mercury under conditions in which the electrons are not in thermal equilibrium with the gas, agrees closely with the value $D_a n = 1.5 \times 10^{18}$ obtained by Mierdel[1] at a vapor temperature of 400°K.

Mierdel found that the electron "temperature," as determined by Langmuir probe measurements, decreased from 6200°K during the discharge to ~2200°K during the first few hundred microseconds of the afterglow and then remained essentially constant. In the present experiment, it is possible to calculate the electron temperature during the afterglow from measured values of the ambipolar diffusion coefficient. According to Eq. (5), if the electrons and ions possess Maxwellian energy distributions of temperatures T_e and T_+, respectively, the ambipolar diffusion coefficient is related to the ionic diffusion coefficient by

$$D_a = D_+(1 + T_e/T_+). \qquad (26)$$

In Sec. IV the ambipolar diffusion was measured under conditions such that $T_e = T_+ = 350°$K. In this case the ionic diffusion coefficient may be calculated directly; the value $D_+ n = 1.8 \times 10^{17}$ (cm^2/sec)(atoms/cc) is obtained. For the case of measurements of ambipolar diffusion in pure mercury, it is assumed that the ions are in thermal equilibrium with the gas even though the electrons are not, i.e., $T_e > T_+ = T_{\text{gas}} = 350°$K. Equation (26) then yields the value $T_e = 2400°$K for the electron temperature during the afterglow, agreeing within experimental error with Mierdel's probe measurements.

Mierdel attributes the rapid decay of electron temperature at the beginning of the afterglow to inelastic collisions between electrons and mercury atoms. It is doubtful whether this mechanism can account for a threefold decrease in electron energy (from $T_e = 6200°$ to 2200°) since only electrons with energies in excess of 4.67 ev (the first excitation potential of mercury) can make inelastic collisions. While such inelastic collisions would rapidly deplete the high energy tail of the electrons' energy distribution, they would have little effect in changing the average energy of the distribution. In Sec. II, it was shown that the energy decay time due to *elastic* collisions is greater than 10^{-3} sec in these experiments. Thus, neither elastic nor inelastic collisions of electrons with mercury atoms can account for the rapid decay of electron energy after the discharge is terminated.

We propose that the transport of energy to the walls of the container by the diffusing electrons is responsible for the energy decay. In the case of ambipolar diffusion, electrons must diffuse against the ambipolar space charge field. Only those electrons which have sufficient kinetic energy to surmount the potential barrier of the space charge well are able to diffuse to the walls. Thus, the large diffusion loss of electrons at the beginning of the afterglow results in the rapid energy decay.

The fact that the electron temperature levels off at ~2200°K, rather than continuing to decrease during the afterglow, suggests the action of a process which

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[23] J. H. Coulliette, Phys. Rev. 32, 636 (1928).

[24] A. O. McCoubrey, Phys. Rev. 84, 1073 (1951).

* *Note added in proof:* A. V. Phelps (private communication) has recently measured the lifetimes of metastable atoms by combined optical absorption and microwave techniques. He finds that in some cases the microwave studies lead to erroneously large values for the metastable de-excitation cross section.

replaces the fast electrons lost by diffusion to the walls. Mierdel suggests collisions of the second kind between slow electrons and metastable atoms as the source of the fast electrons. He attempts to demonstrate the plausibility of such a process by an energy balance argument in which he equates the energy gained by the electrons from collisions with metastable atoms to the energy lost in elastic recoil collisions with normal atoms. There are two objections to this argument: First, Mierdel's probe curves show that the electron temperature becomes essentially constant a few hundred microseconds after the discharge is interrupted. Since the elastic recoil time is several milliseconds, the equilibrium electron temperature resulting from his energy balance process would not be attained with sufficient rapidity. Second, the fast electrons (~ 5 ev energy) produced by collisions of the second kind would diffuse to the walls before losing appreciable energy by elastic recoil, and hence the loss of energy by diffusion would probably determine the energy balance.

In the present experiment in which electrons are produced during the afterglow by metastable-metastable collisions, the electrons' initial kinetic energy is 0.5 ev [the excess energy of reaction (23)]. The subsequent diffusion of these electrons against the ambipolar space charge field may reduce their kinetic energy to the point where their average kinetic energy is 0.3 ev ($T_e = 2400°\mathrm{K}$), the value calculated from the diffusion coefficient measurements. Calculations of electron energy distributions in the presence of space charge fields are not sufficiently advanced to permit quantitative estimates of these effects.[25]

VII. SUMMARY

Studies of electron production and removal in gases of large molecular weight are complicated by the fact that the electrons may not attain thermal equilibrium with the gas during afterglow measurements. This difficulty has been overcome by adding helium to these gases to reduce the electron energy decay time. In the present experiment, measurements have been made of the behavior of thermal electrons in a mercury-helium mixture. At 290°K, it is found that the ambipolar diffusion coefficient of Hg^+ ions and electrons in helium is given by $D_a n = 2.6 \times 10^{19}$ (cm^2/sec)(atoms/cc). The temperature dependence of the diffusion coefficient over the measured range, 290–355°K, agrees with theoretical predictions based on polarization interaction between mercury ions and helium atoms. The ambipolar diffusion coefficient of Hg^+ ions and thermal electrons in mercury is $D_a n = 3.6 \times 10^{17}$ (cm^2/sec)(atoms/cc) at 350°K. These diffusion coefficients agree with values obtained from other experiments[12] and from theory.[14]

It is found that Hg^+ ions are converted to $\mathrm{Hg}_2{}^+$ ions as a result of three-body collisions involving a mercury atom and a helium atom. The frequency of conversion is equal to 140 $(p_{\mathrm{Hg}} \cdot p_{\mathrm{He}})$ sec^{-1}. The formation of molecular mercury ions in the afterglow leads to recombination between the ions and electrons. The measured recombination coefficient is 5.5×10^{-7} cc/sec at 400°K, which is the same order of magnitude as found in noble gases.[21]

Ionization by the collisions of pairs of mercury metastable atoms has been studied in pure mercury. The diffusion coefficient of the $^3P_2$ metastable is given by $D_m n = 1.5 \times 10^{18}$ (cm^2/sec)(atoms/cc) at 350°K. This value is approximately the same as has been found for the $^3P_0$ metastable.[23,24] The measured de-excitation cross section for $^3P_2$ metastables is $\sigma_d = 8 \times 10^{-17}$ cm^2. The electron "temperature" during the afterglow in pure mercury is estimated to be 2400°K. Since the electrons produced as a result of metastable-metastable collisions have initial kinetic energies of 0.5 ev, the estimated electron temperature appears reasonable.

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[25] Preliminary results of such calculations have been reported by I. B. Bernstein and T. Holstein, Phys. Rev. 84, 1074 (1951).