Positive Ions in the Afterglow of a Low Pressure Helium Discharge*

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(Received December 26, 1951)

The production and loss of He^+ and He_2^+ ions in the afterglow of a low pressure helium discharge are studied using a mass spectrometer to analyze the positive ions and microwave techniques to determine the electron density. The change of positive ion and electron density with time is explained by considering three dominant processes in the afterglow: the production of He^+ ions and electrons by collisions between pairs of metastable atoms, the ambipolar diffusion of the ions and electrons, and the conversion of He^+ ions to He_2^+ ions by three-body collisions with neutral atoms. The time constants for the decay of the electron density at low pressures yield the ambipolar diffusion coefficient for He^+ ions of 560 cm²/sec and a frequency for the conversion of He^+ ions into He_2^+ ions of 65 sec^{-1}, both at 1 mm pressure and 300°K. The mobility coefficient for He^+ ions in helium obtained from the measured ambipolar diffusion coefficient is 14 cm²/volt-sec at 300°K and 760-mm pressure and agrees satisfactorily with the value of 12 cm²/volt-sec calculated using the quantum-mechanical interaction of the He^+ ion and the neutral helium atom.

I. INTRODUCTION

RECENT measurements of the ambipolar diffusion coefficient[1] and the drift velocity[2] of helium positive ions in helium have yielded respective mobility values of 13.7 and 12 cm²/volt-sec at 300°K and 760 mm. These values are in agreement with the theoretical value of 12 cm²/volt-sec obtained using a quantum mechanical evaluation of the interaction between atomic helium ions and neutral helium atoms.[3] This agreement provides further indirect evidence in favor of the proposal[4] that the molecular helium ion was responsible for the large mobility value of 22 cm²/volt-sec obtained from previous measurements[5] of the drift velocity of helium ions. The experiment to be described in this paper was designed to test this hypothesis by providing for simultaneous measurement of the ambipolar diffusion coefficient and identification of the positive ions which reach the walls of the diffusion vessel. The ambipolar diffusion coefficient is obtained from the rate of decay of the electron density during the afterglow of a pulsed helium discharge. The positive ions which diffuse to the walls are analyzed with a mass spectrometer.

II. THEORY OF AFTERGLOW PROCESSES

The important processes in the afterglow of a low pressure helium discharge appear to be the ambipolar diffusion of the positive ions and electrons, the conversion of the helium atomic ions into molecular ions, and the production of ions and electrons as a result of collisions between pairs of metastable atoms. Recombination between electrons and ions is not included in this discussion, since it was not found to be significant under the conditions of these experiments. We will consider first the ambipolar diffusion of electrons and two types of positive ions and then solve for the time dependence of the metastable, atomic, and molecular ion, and electron concentrations.

The loss of positive ions and electrons to the walls of the discharge vessel is found by solving for the flow of particles under the action of the combined density gradients ∇n and the space charge field $\mathbf{E}$. The particle current densities $\mathbf{\Gamma}$ are

$$\mathbf{\Gamma}_-=-D_-\nabla n_- -\mu_-\mathbf{E}n_-, \quad \mathbf{\Gamma}_1=-D_1\nabla n_1+\mu_1\mathbf{E}n_1,$$

and

$$\mathbf{\Gamma}_2=-D_2\nabla n_2+\mu_2\mathbf{E}n_2, \tag{1}$$

where the subscripts $-$, 1, and 2 refer to the electrons, atomic ions, and molecular ions, respectively. The D's are diffusion coefficients and the μ's are mobility coefficients. In the limit of large densities of charged particles, the difference density required to maintain the space charge field is small; i.e., $n_1+n_2-n_-\ll n_-\approx n_1+n_2$. The particle currents may then be assumed to satisfy the condition of $\mathbf{\Gamma}_1+\mathbf{\Gamma}_2=\mathbf{\Gamma}_-$. If it is also assumed that the spatial distributions of the ions and electrons are the same so that $\nabla n_1/n_1=\nabla n_2/n_2=\nabla n_-/n_-$, the solution for the electric field from Eqs. (1) is

$$\mathbf{E}=\frac{D_1n_1+D_2n_2-D_-n_-}{\mu_1n_1+\mu_2n_2+\mu_-n_-}\frac{\nabla n_-}{n_-}. \tag{2}$$

As the diffusion and mobility coefficients for the positive ions are small compared to those for the electrons, Eq. (2) reduces to

$$\mathbf{E}=-(D_-/\mu_-)(\nabla n_-/n_-). \tag{3}$$

Substitution of Eq. (3) into Eqs. (1) gives

$$\mathbf{\Gamma}_1=-[D_1+\mu_1(D_-/\mu_-)]\nabla n_1=-D_{a1}\nabla n_1$$

and

$$\mathbf{\Gamma}_2=-[D_2+\mu_2(D_-/\mu_-)]\nabla n_2=-D_{a2}\nabla n_2. \tag{4}$$

These equations show that the two types of ions diffuse

* This work has been supported in part by the Signal Corps, the Air Materiel Command, and the ONR.
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[1] M. A. Biondi and S. C. Brown, Phys. Rev. **75**, 1700 (1949).
[2] J. A. Hornbeck and G. H. Wannier, Phys. Rev. **82**, 458 (1951).
[3] H. S. W. Massey and C. Mohr, Proc. Roy. Soc. (London) **A144**, 188 (1934).
[4] R. Meyerott, Phys. Rev. **70**, 671 (1946).
[5] A. M. Tyndall and C. F. Powell, Proc. Roy. Soc. (London) **A134**, 125 (1931).

independently of each other with ambipolar diffusion coefficients D_{a1} and D_{a2} which are characteristic of the respective ions. These current equations will be substituted into the continuity equations for the two ions and solutions obtained for the positive ion densities as a function of time. The electron density is found by adding the positive ion densities.

The production of ions and electrons as a result of collisions between pairs of metastable atoms according to the reaction $He^M+He^M\rightarrow He^+ + e + He$ has been studied by Biondi.[6] The observed variation of the electron density with time was found to be consistent with the assumption that the loss of metastables by diffusion to the walls and by some unspecified linear volume loss was large compared to the loss due to metastable-metastable collisions. The rate of increase of the metastable concentration is

$$\partial M/\partial t = D_M \nabla^2 M - GM, \tag{5}$$

where M is the metastable concentration, D_M is the diffusion coefficient, and G is the volume loss coefficient. If the metastable concentration at the walls of a cylindrical cavity of height L and radius R is assumed to be zero, the solution to Eq. (5) is

$$M = M_{00} \exp(-t/T_M) \cos(\pi z/L) J_0(2.4r/R) = M_0 \exp(-t/T_M), \tag{6}$$

where $1/T_M = D_M/\Lambda^2 + G$, $1/\Lambda^2 = (\pi/L)^2 + (2.4/R)^2$, and the high order diffusion modes have been neglected.

The He^+ ions are assumed to be produced by metastable-metastable collisions and lost by diffusion to the walls and conversion to molecular ions[7] He_2^+, according to the reaction $He^+ + 2He \rightarrow He_2^+ + He$. The rate of increase of the atomic ion concentration is then

$$\partial n_1/\partial t = D_{a1}\nabla^2 n_1 - \eta n_1 + \beta M^2. \tag{7}$$

Here η is the frequency of conversion of atomic ions into molecular ions and βM^2 is the rate of He^+ production by metastables. We will solve Eq. (7) under the assumption that the positive ion density has the same distribution in space as the metastable concentration in Eq. (6). An exact solution shows that the changes in the spatial distribution resulting from the M^2 term produce a negligible effect on the time variation of the positive ion currents and the average electron density. The atomic ion concentration is then given by

$$n_1 = (n_{10}+A)\exp(-t/T_1) - A\exp(-2t/T_M), \tag{8}$$

where n_{10} is the initial atomic ion density,

$$A = \beta M_0^2 (2/T_M - 1/T_1)^{-1} \quad \text{and} \quad 1/T_1 = D_{a1}/\Lambda^2 + \eta.$$

The molecular helium ions produced by conversion from the atomic ions are lost by diffusion to the walls. Thus, the rate of increase of the molecular ion density is given by

$$\partial n_2/\partial t = D_{a2}\nabla^2 n_2 + \eta n_1. \tag{9}$$

The solution to Eq. (9) is

$$n_2 = (n_{20}+Bn_{10}+BC)\exp(-t/T_2) - B(n_{10}+A)\exp(-t/T_1) + B(A-C)\exp(-2t/T_M), \tag{10}$$

where n_{20} is the initial molecular ion density,

$$B = \eta(1/T_1 - 1/T_2)^{-1}, \quad C = \beta M_0^2 (2/T_M - 1/T_2)^{-1},$$

and $1/T_2 = D_{a2}/\Lambda^2$. The electron density is found by adding Eqs. (8) and (10) to get

$$n_- = [n_{20}+Bn_{10}+BC]\exp(-t/T_2) + [1-B][n_{10}+A]\exp(-t/T_1) - [(1-B)A+BC]\exp(-2t/T_M). \tag{11}$$

The positive ion current which diffuses to the cavity wall and into the mass spectrometer is found by substituting Eqs. (8) and (10) into Eqs. (4). For the simple spatial distribution assumed above, the positive ion current densities at the mass spectrometer entrance are $D_{a1}\pi/L$ or $D_{a2}\pi/L$ times the respective ion concentrations.

The smooth curves of Fig. 1 show semilogarithmic plots of the time variation of the electron, He^+ and He_2^+ densities predicted by Eqs. (8), (10), and (11) for a pressure of 3 mm. The constants used for this calculation are: $D_{a1}p = 540$ cm²-mm of Hg/sec, as measured by Biondi and Brown;[1] $D_{a2}p = 840$ cm²-mm of Hg/sec, as calculated from the results of Tyndall and

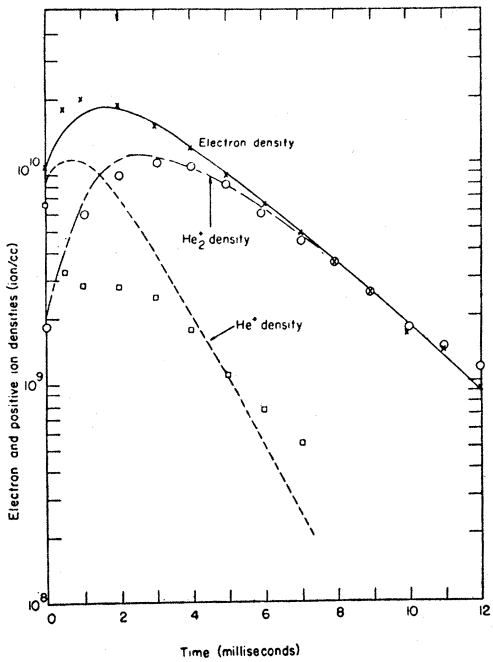

FIG. 1. Theoretical curves and experimental points showing electron, He_2^+, and He^+ densities during the afterglow in helium at 3 mm of Hg pressure.

[6] M. A. Biondi, Phys. Rev. **82**, 453 (1951).
[7] D. R. Bates, Phys. Rev. **77**, 718 (1950).

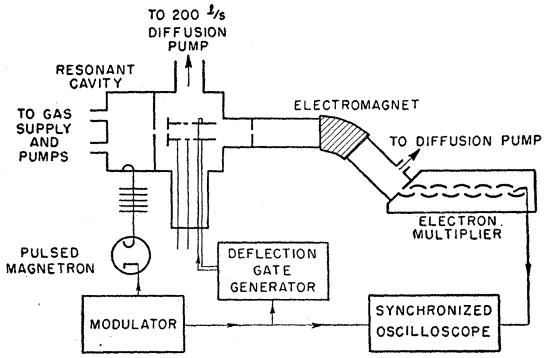

FIG. 2. Block diagram of apparatus used for observing positive ions present during the afterglow.

Powell;[5] $\eta=65p^2$, as found from these experiments; and $D_M p=520$ cm²-mm of Hg/sec and $G=100p$ sec^{-1}, as measured by Biondi.[6] The initial conditions for Fig. 1, $n_{10}=10^{10}$ ions/cc, $n_{20}=2\times10^9$ ions/cc, and $C=2.5\times10^{10}$ cc^{-1}, were chosen to fit the theory to the experimental electron density and molecular ion current curves at $t=0$ and at times late in the afterglow.

III. EXPERIMENTAL APPARATUS

The electron density during the afterglow of the helium discharge was calculated from measurements of the shift in the resonant frequency of the microwave cavity which contained the discharge. The arrangement of the microwave apparatus was the same as that described by Biondi and Brown[1] except that the cavity resonance was indicated by the maximum in the signal transmitted through the cavity.

The positive ions present during the afterglow were observed with the apparatus outlined in Fig. 2. The helium discharge occurs in a microwave cavity resonant at about 10-cm wavelength. A 4-mil diameter hole in the end of the cavity allows some of the ions which diffuse to the wall to enter the focusing region of the mass spectrometer. The gas which enters the spectrometer is removed by a 200 liter/sec oil diffusion pump.

The positive ions are accelerated first in a uniform field region and then in a three-electrode coaxial lens system which focuses the ions on the entrance slit of the spectrometer. The initial accelerating voltage is only 22.5 volts so as to prevent ionization in the intermediate pressure region. A set of deflecting electrodes is provided so as to align the ion beam with the entrance slit. The spectrometer is of the 60° deflection type and has a resolution of about 1 part in 100. The ions leaving the spectrometer are detected with an Allen type electron multiplier,[8] and the relative amplitude of the ion current is determined from the deflection of the trace of a cathode-ray oscilloscope. The modulator of Fig. 2 supplies pulses to the magnetron, the deflection gate generator, and the synchronized oscilloscope. The output of the deflection gate generator is connected to the deflection electrodes of the spectrometer so that by a suitable adjustment of bias voltages the ion current may be prevented from entering the spectrometer except during the 150-μsec gate. A plot of the height of the deflection of the oscilloscope trace during the gate as a function of time gives the time variation of the ion current.

The gas for these experiments is obtained from two-liter flasks of Air Reduction Sales Company spectroscopically pure helium and is supplied to the cavity through a capillary leak and a liquid helium trap. After a baking at about 270°C for several days, the filling system showed a rate of pressure rise of less than 5×10^{-7} mm Hg per hour. Observation with the mass spectrometer showed that at cavity pressures below 1.5 mm of Hg the positive ion current due to impurities was negligible throughout the afterglow. At the highest usable cavity pressures, about 5 mm, the impurity positive ion current reached as much as 10 percent of the helium ion current at times of the order of 15 milliseconds after the end of the discharge. He_3^+ or other complex helium ions were not observed.

IV. RESULTS

The general features of the theory developed above are confirmed by the measured electron density and ion currents as a function of time. The oscilloscope traces of the ion currents at various pressures as illustrated by the photographs of Fig. 3 show that the dominant ion changes from He^+ to He_2^+ as the pressure is increased from 1 to 5 mm. A more detailed comparison of the theory and experiment is possible when the ion

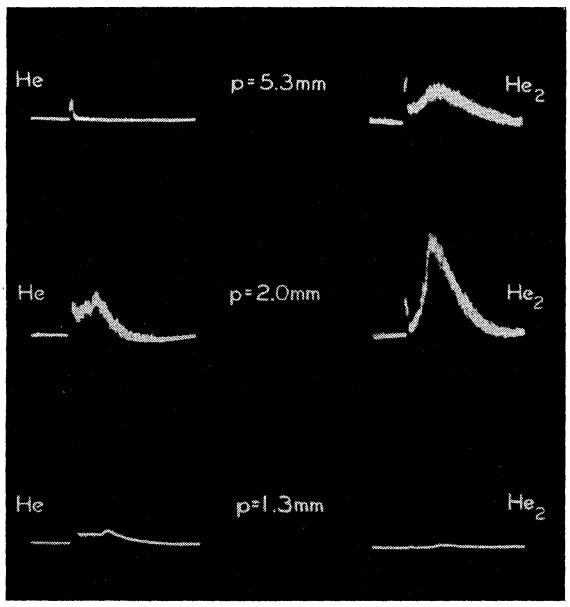

FIG. 3. Oscilloscope traces of helium ion currents as a function of pressure.

[8] J. S. Allen, Proc. Inst. Radio Engrs. 38, 346 (1950).

current reaching the detector during the deflection gate is plotted along with the electron density measurements. In Fig. 1 the experimental ion current data are fitted to the electron density data at times late in the afterglow. The He^+ ion current readings are increased by the ratio of D_{a2}/D_{a1} so as to give curves of relative ion density rather than relative ion current and to make possible a direct comparison of theory and experiment. The experimental time variation of the electron and molecular ion densities is in general agreement with the theoretical curves. The atomic ion curve differs from the theoretical curve in shape as well as magnitude. Possible sources of the discrepancy in magnitude are differences in the sensitivity of the mass spectrometer and electron multiplier detector for atomic and molecular ions. As yet there is no satisfactory explanation for the discrepancy in the final slope of the He^+ ion current curve.

Equation (11) shows that the final decay of the electron density is determined by the time constant for the slowest loss process. This fact means that the electron density measurements can be used for quantitative determinations of the time constant for the loss of He^+ ions at low pressures where $T_1 > T_2 > T_M/2$. From Eq. (7)

$$1/T_1 = D_{a1}/\Lambda^2 + \eta = (D_{a1}p)/p\Lambda^2 + \zeta p^2, \qquad (12)$$

where $D_{a1}p$ and ζ are independent of pressure. This equation shows that a plot of p/T_1 *vs* p^3 should give a straight line with a slope ζ and intercept $D_{a1}p/\Lambda^2$ at zero pressure. Figure 4 shows such a plot for data taken with cavities for which $\Lambda^2 = 0.31$ cm^2 and $\Lambda^2 = 0.85$ cm^2. The average results are $D_{1a}p = 560 \pm 20$ (cm^2-mm of Hg)/sec and $\zeta = 65 \pm 15$ sec^{-1} (mm of Hg)$^{-2}$. The ambipolar diffusion coefficient determined by this method is in very good agreement with the value of 540 ± 10 (cm^2-mm of Hg)/sec reported by Biondi and Brown.[1] The leveling off of the p/T curves at high pressures indicates that the loss of He_2^+ ions has become slower than the loss of He^+ ions, i.e., $T_2 > T_1$. This transition occurs at very nearly the pressure predicted using the constants given in Sec. II.

If we make use of the fact that the electrons should reach thermal equilibrium with the gas within a few hundred microseconds after the discharge is turned off, the ambipolar diffusion coefficient is related to the positive ion mobility[1] by $D_a = 2D_+$ and $\mu_+ = D_+e/kT$. Here k is Boltzmann's constant and T is the absolute gas temperature. The mobility calculated from the above value of D_a is 14 cm^2/volt-sec at 300°K and 760 mm. Thus we conclude that the quantum-mechanical value of 12 cm^2/volt-sec for the mobility of the He^+ ion in helium obtained by Massey and Mohr[3] is in satisfactory agreement with experiment. Possible sources of the small discrepancy are the overestimation of the effects of charge transfer and a departure from the ambipolar condition near the walls of the microwave cavity.

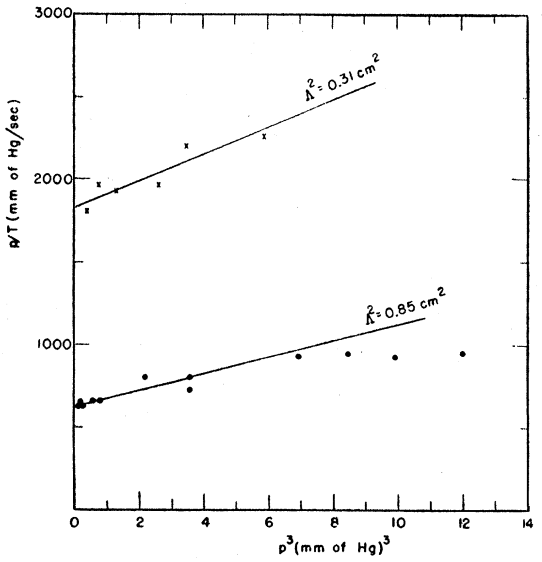

FIG. 4. p/T *vs* p^3 plot for determination of He^+ diffusion and ion conversion rates.

The frequency of conversion of the atomic ions into molecular ions is between one-half and one-third the value predicted by Bates.[7] This discrepancy is not considered significant in view of the approximations made in solving this three-body collision problem using the Thomson recombination theory.[9] The measured rate for this reaction is about twice that found[10] for the similar reaction, $3H \rightarrow H_2 + H$. The rate of formation of He_2^+ given above is about five times the value estimated by Johnson, McClure, and Holt[11] from studies of the light output of the helium afterglow at a pressure of 27 mm.

[9] J. J. Thomson, Phil. Mag. **47**, 337 (1924).
[10] I. Amdur, J. Am. Chem. Soc. **60**, 2347 (1938).
[11] Johnson, McClure, and Holt, Phys. Rev. **80**, 376 (1950).

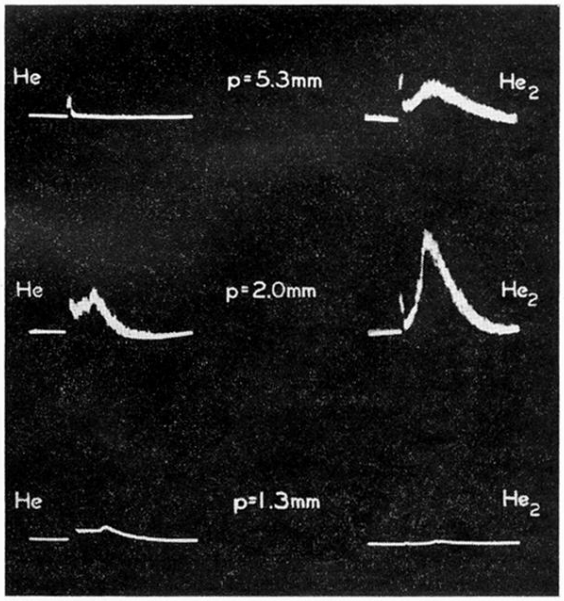

FIG. 3. Oscilloscope traces of helium ion currents as a function of pressure.