(3.26). Now, the lowest-order terms given by (3.29) are identical with the Hamiltonian obtained by Thellung and Ziman in which the first term is the kinetic part of the phonon Hamiltonian, the second term is the roton Hamiltonian, and the third term describes the interactions of phonons with rotons. The Hamiltonian H_Q represents purely quantum-mechanical effects which cannot be obtained from the quantization of the classical hydrodynamic equations. In addition, the Hamiltonian contains the two-particle potential and hence the present formalism is much more related to the microscopic theory.

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[*] This research was supported in part by the Science Development Program of the National Science Foundation, Grant No. SDP-GU-1557.

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[6] In this paper we set $m=1$, $\hbar=1$.

[7] Recently, Fanelli and Struzynski [Phys. Rev. 182, 363 (1969)] have given a proof that Landau's fluid velocity operator, expressed in terms of inverse canonical field operators, has a vanishing curl. However, in the present approach the irrotational condition is regarded as a separate condition for the reasons discussed in the text.

[8] H. Lamb, Hydrodynamics (Cambridge University Press, Cambridge, England, 1932) 6th ed., p. 248.

[9] See, for instance, Ref. 4.

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Production of He$^+$ Ions by Mutual Collisions between Metastable Helium Atoms*

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The time dependence of the He$^+$ ion density has been studied during the decay period of plasmas produced in helium and helium containing 5×10^{-3} % neon. The results show that during the early afterglow period the time dependence of the He$^+$ density is determined by the He$^+$ loss processes, while during the late afterglow period this time dependence may be governed by He$^+$ production due to mutual collisions between triplet metastable helium atoms. The experimental conditions for observing the influence of the He$^+$ production process on its decay rate are discussed.

I. INTRODUCTION

The important role which metastable excited particles may play as a source of ionization during the decay period of a plasma has been recognized for a long time. The occurrence of ionizing mutual collisions between metastable helium particles was postulated by Biondi[1,2] in 1951 to explain an increase in electron density during the early afterglow period of a pure helium plasma. He showed by irradiation of the afterglow that at least part of the ionization during the early afterglow period was due to the helium singlet metastable atoms.

Phelps and Brown[3] were the first to observe He$^+$ and He$_2^+$ mass spectrometrically during the helium afterglow. The final decay rate of He$^+$ at a pressure of 3 Torr was slower than that due to loss processes. Gerber, *et al.*[4] observed the same phenomenon for helium pressures larger than about 4 Torr and mentioned that the deviation from the expected behavior may be due to production of He$^+$ by mutual collisions between metastable helium atoms.

Recently, Collins and Hurt[5] reported electron density, light emission, and absorption studies during the decay period of a plasma produced in helium at a pressure of 3 Torr. These authors concluded from their studies that the production of He$^+$ ions during the late afterglow period was most probably caused by mutual collisions between He$_2(2^3\Sigma_u^+)$ metastable molecules.[6]

The present paper describes mass-spectrometric studies of decaying plasmas produced in helium and a helium-neon mixture. These studies show that the decay rate of He$^+$ during the late afterglow period is governed by production of He^+ by mutual collisions between $He(2^3S)$ metastable atoms.

II. EXPERIMENTAL METHOD

The experimental tube used to study the time dependence of the ions during the afterglow period is shown in Fig. 1. It consists of a differentially pumped mass spectrometer which samples ions diffusing to the walls of the discharge tube. The mass spectrometer used is of the electric-quadrupole type and has been described in detail elsewhere.[7]

The discharge region is a glass cylinder with metal end plates. One end plate is a molybdenum electrode, while the other is made of Kovar metal and contains a small hole (60-μ diameter and 20-μ length) through which the ions effuse into the mass-spectrometer region.

The gas-handling system is analogous to that developed by Alpert.[8] The ultimate pressure was about 10^{-9} Torr following a system bakeout at 350°C for a period of 24 to 36 h. All research-grade pure gases admitted to the discharge region were purified by means of the cataphoretic segregation method.[9] For the studies of plasmas produced in gas mixtures each gas was separately cataphoretically purified before mixing. The final cleaning of the discharge region was achieved by covering the discharge tube wall with a molybdenum layer obtained from sputtering the discharge electrode. This cleaning process was continued until the impurity ion signal was less than 0.5% of that of the dominant ion. This condition was necessary to achieve reproducibility of the data. The gas pressure was measured by a capacitance manometer which controlled a servo-operated valve to maintain a constant preset pressure in the discharge tube.

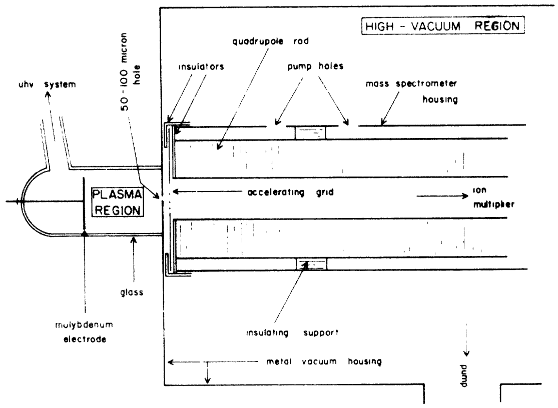

FIG. 1. Plasma container with quadrupole mass-spectrometer ion sampling.

A block diagram of the measuring system is shown in Fig. 2. The discharge was produced by a high-voltage dc pulse applied between the discharge tube electrodes. The ions passing through the quadrupole mass spectrometer are detected by a 14-stage ion multiplier. The resulting anode pulses, each due to a single ion, are amplified by a wideband amplifier and those above a minimum pulse height are selected by a discriminator in order to reduce the background count rate. The pulses from the discriminator are then fed into a multichannel scaler. The afterglow is divided into 100 to 400 equal time intervals which have a minimum duration of 25 μsec. As the multichannel scaler advances from channel to channel, the numbers of pulses in the corresponding time intervals in the afterglow are recorded in the memory section. By accumulating the afterglow counts for a sufficient number of afterglow repetitions, a statistically significant number of counts can be recorded in each channel of the memory. This detection method is considerably faster than the previous sampling method, which consisted of a pulsed-ion multiplier, an RC integrating network and an electrometer, and has also increased the system sensitivity.

III. RELEVANT AFTERGLOW PROCESSES AND THEORY

The most direct method to obtain information about the production process of He^+ ions is the measurement of the time dependence of the He^+ number density under conditions where the production process controls the decay rate. In order to determine the production process and the ex-

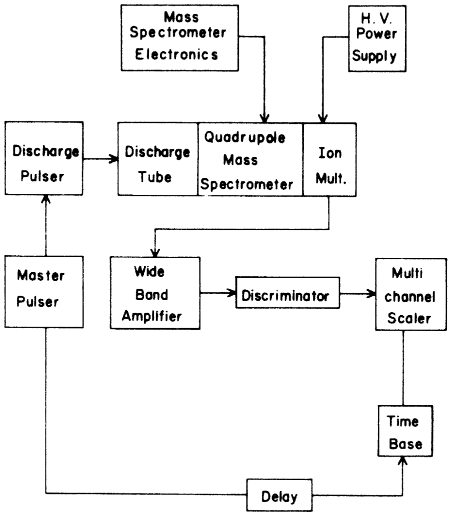

FIG. 2. Block diagram of measuring system.

perimental conditions for which the decay rate of He$^+$ is governed by its production due to mutual collisions between metastable helium atoms and/or molecules the rate equations for both the metastable particles and the positive ions must be solved. The experimental results then can be compared with the predicted decay rates of He$^+$ and the type of metastable particle responsible for the production of He$^+$ can be determined.

A. Helium

Phelps and Brown[3] have derived the equations describing the time dependence of the helium ions and the helium metastable particles for experimental conditions such that:

(1) He$^+$ ions are lost by ambipolar diffusion towards the plasma container walls and by conversion into He$_2^+$ ions by the process

$$\mathrm{He}^+ + 2\mathrm{He} \rightarrow \mathrm{He}_2^+ + \mathrm{He}. \tag{1}$$

(2) He$^+$ ions are produced by the ionization process

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

where M is an as yet unspecified metastable helium particle.

(3) He$_2^+$ ions are lost by the ambipolar diffusion process and are produced by process (1).

(4) The particles M are lost by diffusion towards the walls and by linear volume processes, while the loss due to process (2) has a negligible influence on the rate of disappearance of M.

(5) The production of He$_2^+$ ions by a process analogous to process (2) is absent or negligible and the loss of M due to inelastic collisions with electrons can be neglected.

(6) The loss of He$^+$ and He$_2^+$ by recombination with electrons has a negligible influence on the rate of disappearance of these ions.

The continuity equations of the metastable particles and ions are then given by

$$\frac{\partial M(\vec{r},t)}{\partial t} = D_M \nabla^2 M(\vec{r},t) - \nu_d M(\vec{r},t), \tag{3}$$

$$\frac{\partial n_1(\vec{r},t)}{\partial t} = D_{a_1} \nabla^2 n_1(\vec{r},t) - \nu_c n_1(\vec{r},t) + \beta M^2(\vec{r},t), \tag{4}$$

$$\frac{\partial n_2(\vec{r},t)}{\partial t} = D_{a_2} \nabla^2 n_2(\vec{r},t) + \nu_c n_1(\vec{r},t) . \tag{5}$$

Here, M, n_1, and n_2 are the densities of metastable helium particles, atomic ions, and molecular ions, respectively; D_M is the diffusion coefficient of M, while D_a is the ambipolar diffusion coefficient; ν_d is the volume destruction frequency of M, while ν_c is the frequency of conversion of He$^+$ into He$_2^+$ by process (1); finally, βM^2 is the rate of production of He$^+$ ions by process (2).

The boundary condition of zero densities at the plasma container walls results in the following time dependences of the fundamental diffusion modes[3]:

$$M(0,t) = M(0,0)e^{-t/\tau_m} , \tag{6}$$

$$n_1(0,t) = [n_1(0,0) - A]e^{-t/\tau_1} + Ae^{-2t/\tau_m} , \tag{7}$$

$$n_2(0,t) = [n_2(0,0) + Bn_1(0,0) - BC]e^{-t/\tau_2} - B[n_1(0,0) - A]e^{-t/\tau_1} + B(C-A)e^{-2t/\tau_m} , \tag{8}$$

with

$$1/\tau_M = D_m/\Lambda^2 + \nu_d , \tag{9}$$

$$1/\tau_1 = D_{a_1}/\Lambda^2 + \nu_c , \tag{10}$$

$$1/\tau_2 = D_{a_2}/\Lambda^2 , \tag{11}$$

and

$$A = \frac{\lambda\beta M^2(0,0)}{1/\tau_1 - 2/\tau_m} , \quad B = \frac{\nu_c}{1/\tau_1 - 1/\tau_2} , \tag{12}$$

$$C = \frac{\lambda\beta M^2(0,0)}{1/\tau_2 - 2/\tau_m} .$$

The characteristic diffusion length Λ of the plasma container is for a cylinder with radius R and length L given by

$$1/\Lambda^2 = (2.4/R)^2 + (\pi/L)^2 . \tag{13}$$

The constant λ appearing in the expressions (12) depends on the shape of the plasma container and is the coefficient of the fundamental mode in the expansion in eigenfunctions of the square of the fundamental mode distribution function of the metastable particles. For a rectangular cylinder $\lambda = 0.63$.[10]

For a given value of Λ the values of $2p_0/\tau_m$, p_0/τ_1, and p_0/τ_2 determining the time dependences of He$^+$ and He$_2^+$ can be calculated using published experimental data for the other quantities. Figure 3 shows for $\Lambda^2 = 0.185$ cm^2 the 2 p_0/τ_m values for the metastable helium atoms He(2^1S) and He(2^3S) and for the metastable molecule He$_2$($2^3\Sigma$). The values used for $D_m p_0$ and ν_d were those reported by Phelps.[11]

The values

$$D_{a_1} p_0 = 430 \text{ cm}^2 \text{ Torr sec}^{-1},$$

$$D_{a_2} p_0 = 650 \text{ cm}^2 \text{ Torr sec}^{-1},$$

and $\nu_c = 78\,p_0^2$ sec^{-1} measured during the present experiment were in agreement with previously published data[4] and were used to calculate the values of p_0/τ_1 and p_0/τ_2 as shown in Fig. 3.

Figure 3 makes it possible to determine the pressure above which the final decay rate of He$^+$ is determined by production due to process (2), i.e., the value of p_0 such that $p_0/\tau_1 > 2p_0/\tau_m$. This pressure depends on the type of metastable particle involved. For He$_2$(2$^3\Sigma$) the helium pressure must be larger than 2.2 Torr, while for He(2^{3}S) a pressure larger than 3.1 Torr is required. From Fig. 3 it also follows that it is unlikely that He(2^{1}S) metastable atoms are responsible for the observed production of He$^+$ during the late afterglow period. It appears thus that a measurement of the time dependence of He$^+$ at a pressure sufficiently above 3.1 Torr should make it possible to decide if He$_2$(2$^3\Sigma$) or He(2^{3}S) is the source of the production of He$^+$.

B. Helium-Neon Mixture

The rate constants for the excitation transfer process

$$M + \mathrm{Ne} \rightarrow \mathrm{He} + \mathrm{Ne}^*, \qquad (14)$$

where Ne* is an unspecified excited state of neon, are considerably different for the different metastable helium particles.[12] Therefore, the study of the He$^+$ production process (2) in helium containing a small concentration of neon atoms should also give information about the identity of M.

The time dependence of the charged-particle densities in helium-neon mixtures are influenced by the following ion conversion processes[13]:

$$\mathrm{He}_2^+ + \mathrm{Ne} \rightarrow \mathrm{Ne}^+ + 2\mathrm{He}, \qquad (15)$$

$$\mathrm{Ne}^+ + 2\mathrm{He} \rightarrow (\mathrm{HeNe})^+ + \mathrm{He}, \qquad (16)$$

$$\mathrm{Ne}^+ + \mathrm{He} + \mathrm{Ne} \rightarrow \mathrm{Ne}_2^+ + \mathrm{He}, \qquad (17)$$

$$(\mathrm{HeNe})^+ + \mathrm{Ne} \rightarrow \mathrm{Ne}_2^+ + \mathrm{He}\ . \qquad (18)$$

These additional ion loss and production processes as well as the additional loss process (14) for M can be incorporated in the continuity equations of these particles. The procedure is completely analogous to that leading to the set of Eqs. (6)–(12) and will be omitted here for the sake of brevity.

The values p_0/τ_m, p_0/τ_1, and p_0/τ_2 relating to M, He$^+$, and He$_2^+$ are shown in Fig. 4 as a function of helium pressure for an admixed concentration of 5×10^{-3}% neon. The sharp increase in p_0/τ_2 is due to process (15) for which Oskam[13] reported a rate constant of 1.5×10^{-10} cm^{3}sec^{-1} leading to a conversion frequency of $270\,p_0$ sec^{-1} for the mixture used.[14] The p_0/τ_m values for He$_2$(2$^3\Sigma$) and He(2^{3}S) were calculated from data reported by Phelps.[11,12] The large difference in the p_0/τ_m values for these two different metastable particles for pressures larger than 5 Torr should make it easy to identify the metastable helium particle responsible for the He$^+$ production during the later part of the afterglow period.

IV. RESULTS AND DISCUSSION

The discussion in the previous section gives the experimental conditions under which the production of He$^+$ due to mutual collisions between metastable helium particles should be observed for plasmas produced in both helium and helium containing 5×10^{-3}% neon.

Figure 5 shows the time dependence of the He$^+$ density in helium at a pressure of 5.8 Torr dur-

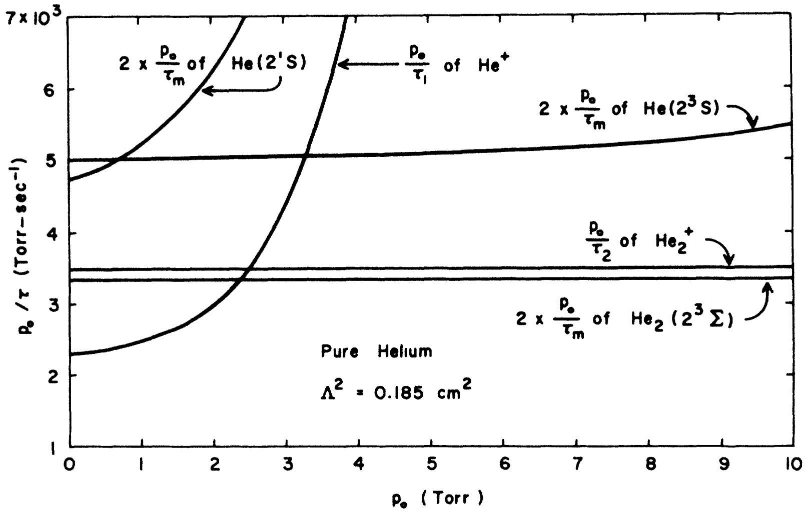

FIG. 3. Calculated values in helium of $2p_0/\tau_m$, p_0/τ_1, and p_0/τ_2 for the metastable particles He (2^{1}S), He (2^{3}S), He$_2$ (2$^3\Sigma$), and the ions He$^+$ and He$_2^+$, respectively. The data used were obtained from the present measurements and reported values (Ref. 11).

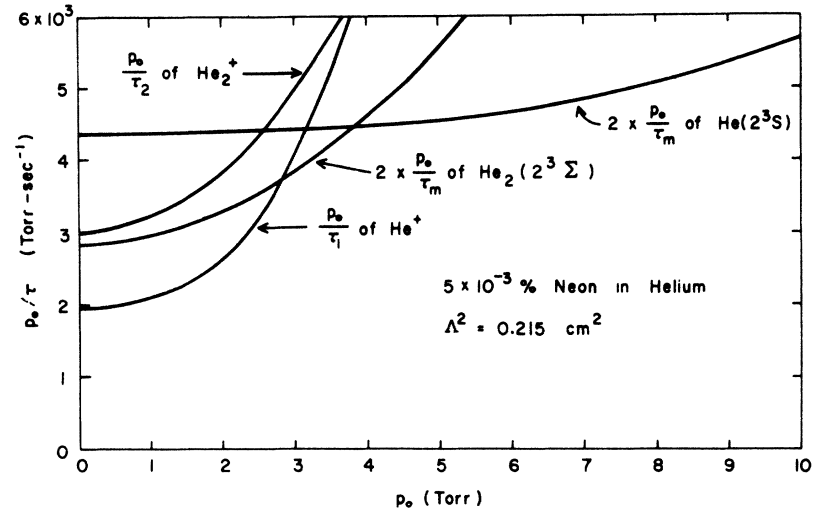

FIG. 4. The same as Fig. 3 but for helium containing 5×10^{-3} % neon.

ing the plasma decay period. The solid line tangential to the early afterglow decay curve is the exponential time dependence expected at this pressure for He^+ loss by ambipolar diffusion and conversion into He_2^+ ions (p/τ_1 curve in Fig. 3). The exponential decay of the He^+ density during the later afterglow period has a p_0/τ value closely equal to $2\,p_0/\tau_m$ of $He(2^3S)$ as shown in Fig. 3. The p_0^3 terms in p_0/τ_1 and p_0/τ_m given in Fig. 5 arise from the quadratic pressure dependences of reaction (1) and of the three-body conversion of $He(2^3S)$ into $He_2(2^3\Sigma)$, respectively. The curve shown in Fig. 5 and analogous curves measured at different pressures show that the metastable particle determining the temporal behavior, i.e., producing He^+, during the later part of the decay period is the $He(2^3S)$ metastable helium atom. If the $He_2(2^3\Sigma)$ metastable molecule was the source of He^+ production the value of $2\,p_0/\tau_m$ would have been 50% larger than the value obtained from the data shown in Fig. 5. This difference is certainly outside the measuring accuracy.

The shape of the decay curve shown in Fig. 5 gives also a justification for neglecting the influence of process (2) on the loss rate of $He(2^3S)$ atoms, since the time dependence of He^+ is an exponential function of time during the late afterglow period. The influence of including a βM^2 loss term in Eq. (3) on the measured decay curve was also calculated by assuming a reasonable value of the initial electron density (10^{11} cm^{-3}). The result of the analysis was that the maximum influence on the He^+ decay rate at the beginning of the afterglow period would only be about 3%, with decreasing influence at later times in the decay period.[15]

The results obtained in helium containing 5×10^{-3} % neon give further proof for the production of He^+ due to mutual collisions between $He(2^3S)$ metastable atoms. The experimental values of p_0/τ relating to the decay rate of He_2^+, which were equal to those of He^+, during the later part of the afterglow period are shown as a function of p_0^3 in Fig. 6. The solid lines represent the maximum error limits of $2\,p_0/\tau_m$ for $He(2^3S)$ and $He_2(2^3\Sigma)$ which follow from the limits reported by Phelps.[10,11] The experimental data are again con-

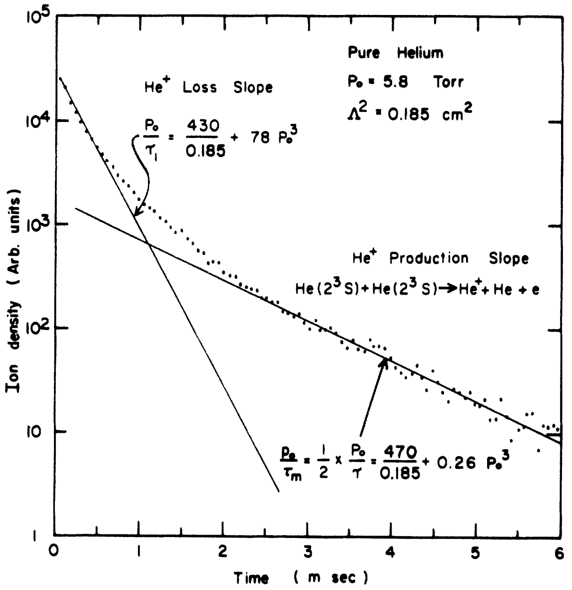

FIG. 5. The time dependence of the He^+ density during the decay period of a plasma produced in helium at a pressure of 5.8 Torr and a gas temperature of 300°K. The final slope is $2p_0/\tau_m$ for $He(2^3S)$ metastable atoms as shown in Fig. 3.

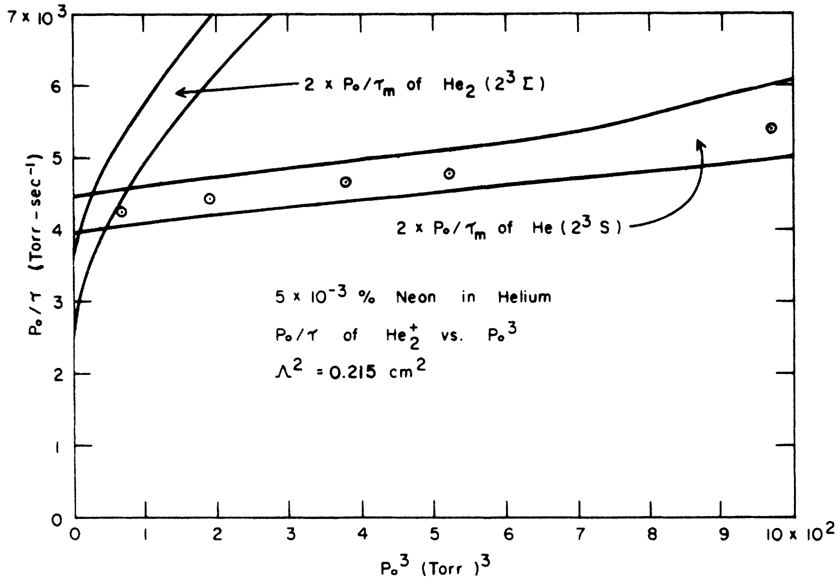

FIG. 6. Measured values of p_0/τ for He^+ and He_2^+ as a function of p_0^3. (Gas temperature 300° K.) The solid-line pairs are those calculated from measured and published data. (Refs. 11 and 12).

sistent with the production of He^+ by mutual collisions between $He(2^3S)$ atoms.

The present conclusions are clearly in disagreement with the conclusion of Collins and Hurt,[5] from their studies performed in pure helium at a fixed pressure of 3 Torr, that the production of He^+ by $He_2(2^3\Sigma)$ metastable molecules is responsible for the time dependence of He^+ during the late afterglow period. Their method of measurement, however, is considerably less direct, since the time dependence of He^+ had to be inferred from atomic light emission intensity and electron-density measurements. Moreover, the decay rate of metastable particle densities, obtained from light absorption studies, are not consistent with the data reported by Phelps.[11]

Additional confirmation of the present results are the mass-spectrometer studies of the helium afterglow reported by Phelps and Brown.[3] These authors could not explain the final decay rate of the measured He^+ density, shown in Fig. 1 of Ref. 3, since it was smaller than predicted by the He^+ loss processes. Recently, Phelps[16] pointed out that the final He^+ decay rate, however, is in perfect agreement with a decay rate controlled by production of He^+ by mutual collisions between $He(2^3S)$ atoms.

Electron-density measurements have shown the production of ions during the early part of the helium afterglow.[1,2] An analogous phenomenon during the late afterglow period was never detected during these studies. This can easily be explained by considering the values of p_0/τ_1, p_0/τ_2, and $2\,p_0/\tau_m$ for $He(2^3S)$ plotted in Fig. 3. The density of electrons is equal to the sum of the positive-ion densities, so that its time dependence is obtained by adding Eqs. (7) and (8). The exponential function corresponding to the smallest p_0/τ value will determine the time dependence of the electron density during the late afterglow period. This will, for small p_0 values, be p_0/τ_1 according to Fig. 3, while for larger p_0 values p_0/τ_2 determines the final decay rate of the electron density. Both time constants relate to loss processes of ions, so that the effect of ionization by metastable particles is not observable by measuring the electron density during the late afterglow period. During the early afterglow period, however, the number of $He(2^1S)$ and $He(2^3S)$ metastable atoms may be large enough to result in a production rate of electrons by process (2) larger than the loss rate of electrons by ambipolar diffusion. Then the electron density will increase with time during the early afterglow period. This type of electron-density time dependence led Biondi[1,2] to postulate the production of He^+ by metastable helium atoms.

The previous discussion with respect to the influence of He^+ production by metastable atoms on the time dependence of the electron density during the late afterglow period does not necessarily hold for helium-neon mixtures. The processes (15)–(18) convert ions having a small electron-ion recombination coefficient (He_2^+ and Ne^+) into an ion having a large recombination coefficient (Ne_2^+). These conversion processes have rather large rate coefficients, as is shown for He_2^+ in Fig. 4, and may for appropriate experimental conditions result for all ions in p_0/τ values related to ion-loss processes larger than $2\,p_0/\tau_m$. Under these conditions the final decay rate of the electron density in helium-neon afterglows is determined by $2p_0/\tau_m$ in contrast with the electron-density decay in pure helium afterglows. A detailed study of decaying plasmas produced in helium-neon mixtures will be published elsewhere.[17]

V. CONCLUSIONS

Studies of the decay rate of He$^+$ ions during the late afterglow period of plasmas produced in helium and a helium-neon mixture have shown that during this period the decay rate is controlled by He$^+$ production due to mutual collisions between He(2^3S) metastable atoms.

The analysis presented is in agreement with previously reported studies of the time dependence of the electron density during the decay period of plasmas produced in helium.[1,2] Moreover, it explains the decay rate of He$^+$ ion density during the later afterglow period as measured by Phelps and Brown.[3,16] The present results, however, are in disagreement with the conclusion of Collins and Hurt[5] that the production of He$^+$ during the later afterglow period is due to mutual collisions between He$_2$($2^3\Sigma$) metastable helium molecules.

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