Recombination of He+ and He++ in the Afterglow of a Helium Discharge*

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Studies of the time dependence of atomic and molecular light intensities, electron density, atomic metastable densities, and electron temperature have allowed the determination of the He+-electron and He++electron recombination coefficients as functions of electron density and temperature. The results are in reasonable agreement with the theory of collisional-radiative recombination. The mechanisms controlling metastable densities and heating of the electron gas are discussed. In particular, the disappearance of the 23S metastable atom seems best explained in terms of collisional de-excitation by electrons.

INTRODUCTION

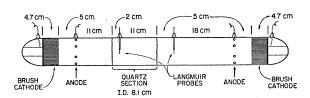
N earlier experiments, using pulsed microwave cavities or waveguides, the observed time dependency of the electron density n was used to ascertain the degree to which the loss processes were dominated by electron-ion volume recombination and, simultaneously, to determine the value of the recombination coefficient itself from a plot of 1/n(t) versus the time t. It has since been shown2 that, in the presence of diffusion, linearity of a 1/n(t)-versus-t plot is neither a guarantee of recombination control nor a good measure of the recombination coefficient, unless the region of linearity is at least a factor of approximately 10 in the electron density. Even in cases where this criterion is met, there are other uncertainties. In general, the radial distribution of electron density was surmised rather than measured and was probably time-dependent. This introduces uncertainty into the interpretation of the frequency shift of the cavity in terms of the spacial average of the electron density. There are, moreover, serious limitations to the electron density region over which the cavity technique can be applied.3 Purity of the gas was an additional problem and, for a while, the measured recombination coefficients became progressively lower as the purity was improved. In all of these early experiments, a dependence of the assumed two-body recombination coefficients on electron density was neither allowed for nor found experimentally. For helium, the theoretical picture was further obscured by the assumption that electron loss proceeded primarily by dissociative recombination of the He₂⁺ ion,⁴ a belief that has persisted until very recently.

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If the above uncertainties were disconcerting when only two-body recombination was to be considered, they are much more so now following the development of the theory of collisional-radiative recombination⁵ since this theory predicts a recombination coefficient which is in most cases strongly dependent on both electron density and electron temperature. Measurements of the recombination coefficient without fairly precise, correlated measurements of the electron density and electron temperature are, therefore, meaningless.

Recent experimental and theoretical developments have shown that recombination in helium cannot be interpreted in terms of a dissociative mechanism. 6 Other recent work^{7,8} is in reasonable agreement⁹ with the theory of collisional-radiative recombination, but further experimental confirmation is clearly needed.

In this experiment, an attempt is made to remove some of the difficulties associated with earlier measurements by moving to a regime where the loss rates are more strongly dominated by recombination and by



PULSED PLASMA TUBE

Fig. 1. Diagram of the plasma tube.

9 D. R. Bates and A. E. Kingston, Proc. Roy. Soc. (London) A279, 32 (1964).

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¹ M. A. Biondi and S. C. Brown, Phys. Rev. **76**, 1697 (1949); R. A. Johnson, B. T. McClure, and R. B. Holt, *ibid*. **80**, 376 (1950); D. E. Kerr, Bull. Am. Phys. Soc. **5**, 372 (1960); D. E. Kerr, Final Summary Report on Transient Studies of Ionization and De-ionization Processes in Gaseous Discharges 1960 (unpublished); ionization Processes in Gaseous Discharges 1960 (unpublished); M. C. Sexton and J. D. Craggs, J. Electron. Control 4, 493 (1958); H. J. Oskam, Phillips Res. Rept. 13, 419 (1958); C. L. Chen, C. C. Leiby, and L. Goldstein, Phys. Rev. 121, 1391 (1961).

² E. P. Gray and D. E. Kerr, Ann. Phys. (N. Y.) 17, 276 (1962).

³ K.-B. Persson, Phys. Rev. 106, 191 (1957).

⁴ D. R. Bates, Phys. Rev. 77, 718 (1950); 78, 492 (1950); M. A. Biondi, *ibid.* 82, 962L (1951); W. A. Rogers and M. A. Biondi, *ibid.* 134, A1215 (1964).

⁶ D. R. Bates, A. E. Kingston, and R. W. P. McWhirter, Proc. Roy. Soc. (London) A267, 297 (1962); A270, 155 (1962); D. R. Bates and A. E. Kingston, Proc. Phys. Soc. (London) 83, 43

<sup>(1964).

&</sup>lt;sup>6</sup> E. E. Ferguson, F. C. Fehsenfeld, and A. L. Schmeltekopf, Phys. Rev. 138, A381 (1965).

⁷ R. W. Motley and A. F. Kuckes, in *Proceedings of the Fifth Invitation in Gases. Munich* (North-⁴ R. W. Motley and A. F. Kuckes, in *Proceedings of the Populational Conference on Ionization in Gases, Munich* (North-Holland Publishing Company, Amsterdam, 1962), p. 651; E. Hinnov and J. G. Hirschberg, Phys. Rev. 125, 795 (1962).

⁸ C. B. Collins, W. B. Hurt, and W. W. Robertson, in *Proceedings and Conference on Electronic and Conference on Electronic and Conference on Proceedings and*

ceedings of the Third International Conference on Electronic and Atomic Collisions, London, 1963 (North-Holland Publishing Company, Amsterdam, 1964), p. 517; F. E. Niles and W. W. Robertson, J. Chem. Phys. 40, 2909 (1964); F. Robben, W. B. Kunkel, and L. Talbot, Phys. Rev. 132, 2363 (1963); R. A. Gerber, G. F. Sauter, and H. J. Oskam, Phys. Letters 19, 656 (1966).

using a more optimum geometry, in this case a cylinder of sufficient diameter that measurements of radial dependence become practical, and of sufficient length that the end effects can be neglected. An extended negative glow discharge¹⁰ was used because it provides a high-energy (~3-keV) electron-beam excitation of the plasma, resulting in a source function which is constant over the volume.11 The result is an experimental situation which is very well suited to the measurement of recombination. A rather high degree of recombination control is assured by the combination of high electron density ($\sim 10^{12} \,\mathrm{cm}^{-3}$), low electron temperature (~ 0.05 to 0.1 eV), and relatively large size (8 cm diam × 50 cm length, corresponding to a fundamental diffusion length $\Lambda = 1.69$ cm). The ratio of the recombination loss rate to the diffusion loss rate in the early afterglow is typically $\sim 5:1$. Furthermore, the ratio of $\text{He}(2^3S)$ to the electron density n is relatively low (1:4 to 1:10) and there is proportionally less influence of 23S metastables during the afterglow. A procedure of analysis is here presented which allows the calculation of the recombination coefficient, in the presence of ambipolar diffusion, from the experimental light intensity and electron density measurements without any assumption as to the specific dependence of the recombination coefficient on electron density.

EXPERIMENTAL PROCEDURE

Figure 1 shows the plasma tube including two brush cathodes, which were operated at high negative potential, and two grounded anodes. The region of the

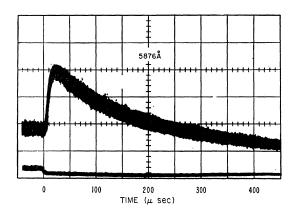


Fig. 2. Intensity of the 5876-Å line of atomic helium as a function of time, $50\,\mu\text{sec/cm}$. The top oscilloscope trace is without external heating of the electrons. For the bottom trace the recombination light is quenched by diathermy radiation at 2450 MHz. In this latter case the light intensity is essentially zero after cutoff of the plasma excitation.

¹⁰ K.-B. Persson, J. Appl. Phys. 36, 3086 (1965); T. D. Roberts, Eighteenth Gaseous Electronics Conference, 1965 (unpublished).
¹¹ That this is so has been confirmed by performing an Abel inversion of a 5016-Å light intensity profile taken while the electron temperature was raised by shining 2450 MHz radiation on the plasma. Thus the recombination light was removed and only 5016-Å light from direct excitation by the electron beam was observed.

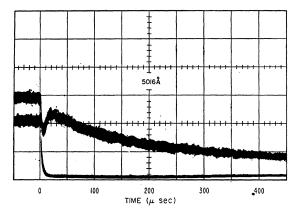


Fig. 3. Intensity of the 5016-Å line of atomic helium as a function of time, $50\,\mu\text{sec/cm}$. As in Fig. 2, the top and bottom oscilloscope traces are, respectively, without and with microwave quenching of the recombination light.

plasma subjected to study was midway between the two anodes and was therefore free of fields except for the space-charge field set up by ambipolar diffusion to the wall. The excitation current, which could be varied between 20 and 100 mA, was monitored by measuring the voltage across a 1- Ω resistor connecting the two anodes to ground. The system was baked at 450°C, after which a vacuum of $\sim 3 \times 10^{-10}$ Torr was indicated. The system was then filled with helium, purified by allowing it to leak into a reservoir through a heated quartz wall.12 In filling the plasma tube from the reservoir, the pressure was measured using a capacitance manometer, calibrated against an oil manometer. Pressures of from 0.7 to 1.2 Torr were used. Spectroscopically, we observed no lines of neon, the major impurity in commercial helium. Any such lines present were of considerably lower intensity than the observed faint FeI impurity lines.

The tube was pulsed 20 to 30 times per sec, the excitation voltage being allowed to build up slowly so that the plasma could come to equilibrium. Thus an on-time of 3 to 5 msec was required. The voltage was then removed abruptly by the use of a thyratron resulting in the disappearance of the excitation current within approximately 3 usec. Although the cathode voltage did not drop quite to zero and hence a slight amount of current continued to flow between cathode and anode, the power involved was very low, dropping from ~200 W during the discharge to less than 4 $\times 10^{-2}$ W, within 100 μ sec and further decreasing to <3×10⁻³ W after 1 msec. Any electrons produced by this residual power input were of energy less than 30 eV and therefore had a relatively short mean free path. Thus even this small amount of power was contained within the cathode-anode regions. Ion production by this residual current was nil since a uniform drop of 30 V or less in 5 cm is incapable of producing ionization in helium at a pressure of 1 Torr.

¹² F. J. Norton, J. Am. Ceram. Soc. 36, 90 (1953).

Five different types of measurement were made on the decaying plasma as a function of time. They are measurements of the spectral line intensity, the projected brightness profile, the electron density, the electron temperature, and the absorption of 3889-Å and other spectral lines. These will be discussed in turn.

The spectral line intensity of several atomic lines, in particular 5876, 3889, 5016, and 4713 Å, corresponding to the $3^3D \rightarrow 2^3P$, $3^3P \rightarrow 2^3S$, $3^1P \rightarrow 2^1S$, and $4^3S \rightarrow 2^3P$ transitions, respectively, were measured as a function of time. There seems to be little or no difference between the time dependence of different atomic lines. Figures 2 and 3 show behavior of the 5876- and 5016-Å lines as a function of time, both with and without heating of the electron gas by diathermy radiation at 2450 MHz. When the electron gas is heated, the recombination coefficient is reduced drastically and the recombination light is extinguished as shown by the fact that the spectral line intensity drops essentially to zero at the time the plasma excitation is cut off. Thus the curves with diathermy heating represent only the light due to direct excitation by beam electrons while the curves without diathermy heating show the light due to both direct excitation and recombination. It is therefore clear from Figs. 2 and 3 that, during the active discharge, approximately 80% of the 5016-Å light results from direct excitation while the 5876-Å light is mainly the result of recombination. As the exciting electron beam is cut off, there is an initial drop in the light intensity due to the removal of direct excitation, followed immediately by a pronounced rise as the electron gas cools thus increasing the recombination coefficient. Subsequently the recombination rate, and hence the light intensity, begin to fall as the electron density decreases. The use of a phase-sensitive amplifier enabled us to extend the measurements to times as late as 11 msec in the afterglow.

Measurements of the projected brightness profile for a given spectral line were made by scanning the spectrometer across the plasma tube. These measurements were made with time resolution using a gate length of 10 to 15 μ sec. In order to determine the radial distribution of volume emission, I(r), the Abel inversion¹³ of these profiles was calculated by a computer program using a series expansion in either Legendre, Tchebycheff, or Gegenbauer ($\alpha = 2$) orthogonal polynomials.^{14,15} The resulting I(r) distributions from extensive sets of projected profiles, showed an initial change during the first 50 to 100 μ sec after which the radial distribution remained essentially constant for at least 2 msec. Thus the light intensity and electron density, measured as averages along a diameter of the plasma tube, can be referred to the values on the axis by correction factors which remain constant from at least 100 µsec to 2 msec.

¹⁵ E. R. Mosburg, Jr. and M. S. Lojko (to be published).

The time development of the radial electron density distribution in a decaying plasma has been calculated by Gray and Kerr.² However, their curves are not directly applicable to this experiment for three reasons. They use only the limiting conditions of an initial recombination distribution or an initial diffusion distribution, they consider only two-body (not three-body) recombination, and their theory does not allow for any variation of α with time due to variations in the electron temperature. A comparison of their Fig. 2 and Fig. 5 indicates that the radial distributions for the two initial conditions tend to converge toward a single distribution within an interval ~ 0.4 diffusion times. This common distribution is probably not far different from the steady-state distribution for a ratio R of recombination loss rate to diffusion loss rate at the center of the plasma, which is equal to that occurring at this time in the afterglow. Although this convergence is neither complete nor rapid, we might expect the afterglow and steady-state distributions to be much more similar in the early afterglow if the initial distribution is the steady-state one rather than either of the extreme limiting cases used by Gray and Kerr. Because of the strong temperature dependence of the recombination coefficient, even a slight decrease in electron temperature with time would suffice to keep R, and hence the radial distribution, constant during part of the afterglow.

In order to determine the steady-state electron density distribution for the present experiment, the equations for diffusion with the recombination loss added were solved on the computer for the case of an electronbeam excited plasma.¹⁶ The resulting radial electron density distributions, n(r)/n(0), for various values of the ratio of recombination loss to diffusion loss, were related to I(r) by the equation $I \propto \alpha(n)n^2$. Here the recombination coefficient $\alpha(n)$ could have any arbitrary dependence on the electron density n, so that any recombination mechanism could be considered. An analysis was made for the two-body, three-body, and collisional-radiative (700°K) recombination mechanisms.

When the resulting radial distributions I(r) are compared with each other,16 it is immediately seen that the shape of the distribution depends mainly on the ratio of recombination loss to diffusion loss and is relatively insensitive to the particular mechanism of recombination being considered. Furthermore, the needed correction factor, which is just the ratio of the electron density at the center to the density averaged along a diameter, is itself fairly insensitive to errors in the ratio R.

Comparisons of these light intensity curves with the experimental curves were used to obtain a first approximation to the value of R. A more reliable determination of R is obtained in the analysis of the data by Eqs. (23)-(27) since $R = y\Lambda^2/D$. The solution could then be iterated if this seemed desirable. The values of R determined in these two ways are in reasonable agreement.

¹³ H. R. Griem, Plasma Spectroscopy (McGraw-Hill Book Com-

pany, Inc., New York, 1964).

14 C. H. Popenoe and J. B. Shumaker, Natl. Bur. Std. J. Res. 69A, 495 (1965)

¹⁶ E. R. Mosburg, Jr., Phys. Fluids 9, 824 (1966).

The resulting correction factors for the electron density were between 1.30 and 1.35. It is very unlikely that they would be in error by more than 10%.

The next measurements we consider are those of electron density, which were made with 10 µsec time resolution using a microwave interferometer at 35 GHz.¹⁷ The microwave beam was collimated by absorbers to a circular cross section of 35-mm diam. Thus the observed phase shift was a measure of the average electron density along a diameter of the plasma tube. Phase shifts of as low as 1° were detectable, corresponding to approximately 1010 electrons per cm3.

The electron temperature T_e was measured by a pulsed Langmuir probe technique¹⁸ in which the probe was pulsed, once in each afterglow period, using a square pulse of approximate duration 10 µsec and of variable height. By manually varying the height of the pulse, a probe curve was thus traced out on an x-yoscilloscope, the trace being brightened during the flat top of the pulse applied to the probe. As mentioned above, the type of plasma¹⁰ used in this experiment has a very low electron temperature. During the active discharge the measured electron temperature is between approximately 1000 and 1200°K. Within the 50-µsec period immediately following the end of the discharge, there is an abrupt decrease in the electron temperature by a factor of between 1.3 and 2. From $100 \,\mu\text{sec}$ to 2 msec the electron temperature remains at a new quasiequilibrium value in the range from 500 to 800°K, considerably above the gas temperature of approximately 300°K.

In order to check the accuracy of such measurements, similar probe curves, taken in the steady-state plasma, were compared with spectroscopic measurements of the electron temperature determined both from the relative light intensity of the high lines (n=10 to n=21) in the $n^3P \rightarrow 2^3S$ series, and from the intensity of the continuum beyond this series limit. Of the two, the continuum measurement was the more precise, with a precision of about $\pm 5\%$ compared to approximately $\pm 15\%$ for the relative line intensity measurement. The precision of the pulsed probe measurement was about $\pm 5\%$. The electron temperatures obtained from the continuum measurements agreed with those obtained from the pulsed probe measurements to within approximately 5 to 10%. Two 75-cm Fastie-Ebert spectrometers were used in tandem in order to reduce the scattered light so that these measurements could be made. Due to the low fractional duty cycle, similar spectroscopic measurements of the temperature with time resolution in a pulsed discharge were not feasible.

Finally, measurements of the absorption of 3889- and 5016-Å radiation by the plasma allowed an estimate of the densities of the 23S and 21S helium metastable atoms.

A water-cooled helium capillary discharge was used as the light source. The technique used for measuring low fractional absorptions was similar to that of Phelps and Pack¹⁹ and the limiting sensitivity of 2×10⁻⁴ was also essentially the same. Fractional absorptions as high as 0.24 were observed for the 3889-Å line, corresponding to a 2^3S metastable density of approximately 2.6×10^{11} cm⁻³, averaged along a diameter. Fractional absorption of 5016-Å light was an order of magnitude lower than this and exhibited a faster time decay. The maximum observed value corresponds to a 2¹S metastable density of approximately 6×10° cm⁻³. These values are subject to possible errors due to the fact that the optical absorption technique measures only the difference between the density of the lower level and that of the higher level connected by the transition.²⁰ There is some experimental indication that, at 100 µsec, the density of the upper level for the 3889-Å transition may not be totally negligible as assumed in this paper. The values given for the metastable densities would then be too small.

Gaussian line shapes were assumed for both the emission profile of the lamp and the absorption profile of the plasma, with the ratio ρ of the absorption width to emission width becoming a parameter of the equation. The solution of the equation shows that, for a given fractional absorption, the calculated metastable density varies by less than a factor of 2 as ρ is varied from 0.5 to 2. The data were analyzed assuming $\rho = 1$.

ANALYSIS OF THE He+ ION RECOMBINATION

In all of the following analysis, it is understood that the function n(t) used in the equations has already been corrected to the value at the axis of the tube by the method outlined under Experimental Procedure.

The differential equations governing the afterglow concentrations of the three major charged components of the plasma are (where a dot over a symbol indicates its time derivative and brackets indicate the densities of the reactant components):

$$\dot{n} = -\alpha(n)n[\text{He}^+] - \alpha_M(n)n[\text{He}_2^+] - \alpha_D(n)n[\text{He}_2^+]$$

$$-\frac{D}{\Lambda^2}[\text{He}^+] - \frac{D_M}{\Lambda_M^2}[\text{He}_2^+] + \gamma[2^3S]^2, \quad (1)$$

$$d[\text{He}^+]/dt = -\alpha(n)n[\text{He}^+] - \frac{D}{\Lambda^2}[\text{He}^+] + \gamma[2^3S]^2$$

$$-\delta[\text{He}]^2[\text{He}^+], \quad (2)$$

$$d[\text{He}_2^+]/dt = \delta[\text{He}]^2[\text{He}^+] - \alpha_M(n)n[\text{He}_2^+]$$

$$-\alpha_D(n)n[\text{He}_2^+] - \frac{D_M}{\Lambda_M^2}[\text{He}_2^+]. \quad (3)$$

¹⁷ A. J. Estin and M. M. Anderson, Rev. Sci. Instr. 37, 468

<sup>(1966).

18</sup> D. G. Bills, R. B. Holt, and B. T. McClure, J. Appl. Phys. 33, 29 (1962).

A. V. Phelps and J. L. Pack, Rev. Sci. Instr. 26, 45 (1955).
 A. C. G. Mitchell and M. W. Zemansky, Resonance Radiation and Excited Atoms (MacMillan Company, New York, 1934),

If dissociative recombination of the He_2^+ ion is for the moment assumed to occur, then the atomic and molecular line intensities are given by

$$I_A = k_A \alpha(n) n \lceil \text{He}^+ \rceil + k_D \alpha_D(n) n \lceil \text{He}_2^+ \rceil, \qquad (4)$$

and

$$I_M = k_M \alpha_M(n) n \lceil \text{He}_2^+ \rceil, \tag{5}$$

where, in general, k_A , k_M , and k_D differ for each line considered and are to some extent temperature-dependent. Other symbols used are the electron density n; the atomic and molecular nondissociative recombination coefficients $\alpha(n)$ and $\alpha_M(n)$, respectively, (expressed in two-body form but actually without any assumption as to their n dependence); the dissociative recombination coefficient $\alpha_D(n)$; the atomic and molecular ambipolar diffusion coefficients D and D_M ; the corresponding diffusion lengths Λ and Λ_M ; and the rate coefficients γ and δ , for the following reactions:

$$\operatorname{He}(2^{3}S) + \operatorname{He}(2^{3}S) \xrightarrow{\gamma} \operatorname{He}^{+} + e + \operatorname{He}(1^{1}S),$$
 (6)

and

$$\text{He}^+ + 2 \text{ He} \xrightarrow{\delta} \text{He}_2^+ + \text{He}.$$
 (7)

Finally, because of local neutrality

$$n = [He^+] + [He_2^+]. \tag{8}$$

We have calculated γ from the relation $\gamma = v\sigma$ using the value²¹ of $\sigma = 1 \times 10^{-14}$ cm², which results in $\gamma = 1.2 \times 10^{-9}$ cm³ sec⁻¹. The value of δ used²² was 1.08×10^{-31} cm⁶ sec⁻¹. These reaction rates depend on the neutral and ion temperatures but not on the electron temperature. On the other hand, the diffusion terms D/Λ^2 depend on the electron temperature and the radial electron density distribution. Fortunately, in our case they are also small relative to the recombination loss term during the early afterglow.

If we further assume, tentatively, that the production of atomic light is *dominated* by the dissociative recombination process, then we may write

$$\frac{\dot{I}_A}{I_A} = \frac{\dot{\alpha}_D}{\alpha_D} + \frac{\dot{n}}{n} + \frac{d[\text{He}_2^+]/dt}{[\text{He}_2^+]}$$
(9)

and

$$\frac{\dot{I}_M}{I_M} = \frac{\dot{\alpha}_M}{\alpha_M} + \frac{\dot{n}}{n} + \frac{d[\text{He}_2^+]/dt}{[\text{He}_2^+]}.$$
 (10)

The difference between these two equations gives

$$\frac{\dot{I}_M}{I_M} - \frac{\dot{I}_A}{I_A} = \frac{\dot{\alpha}_M}{\alpha_M} - \frac{\dot{\alpha}_D}{\alpha_D}.$$
 (11)

The recombination coefficients on the right side have time derivatives only through their dependence on the electron density. Let the recombination coefficients $\alpha_M(n)$ and $\alpha_D(n)$ be proportional to the electron density

raised to the powers p_M and p_D , which then have values between zero and one, corresponding to the limits of two-body and three-body recombination. Therefore the right side of Eq. (11) can be written as $(p_M - p_D)\dot{n}/n$. From the theory of collisional-radiative recombination, one would expect that in the region of electron density and temperature of this experiment, p_M would be close to one. If the assumed dissociative recombination is a two-body process so that $p_D = 0$, then of necessity, since $\dot{n}/n < 0$, the right-hand side of Eq. (11) is less than zero regardless of the *n* dependence of $\alpha_M(n)$. Collins²³ has, however, recently investigated the theory of collisional-dissociative recombination and finds a three-body dependence $(p_D=1)$ over a wider range of nthan for collisional-radiative recombination. This could lead to the possibility of a small positive value for the right-hand side of Eq. (11) if the n dependence of $\alpha_M(n)$ were simultaneously less than first power. Such a value would however, still be much smaller than $-\dot{n}/n$, whose measured value was in turn much less than the measured value of the left side of Eq. (11). Measurements of the atomic and molecular light show that the atomic light disappears much faster than the molecular light so that the left-hand side of Eq. (11) is always positive. During the interval from 50 µsec to several hundred microseconds the typical magnitude is between 10^3 and 2×10^3 sec⁻¹. At a later time (~ 3 msec) this magnitude may drop by a factor of 10 but always remains positive. This tentative assumption that the production of atomic light is dominated by a dissociative recombination mechanism is therefore shown to be inconsistent with our experimental measurements.

In the absence of mass spectrometer measurements, a solution of the equations with appreciable contributions from both dissociative and nondissociative recombination is very difficult. We have seen that an analysis assuming dominance of atomic light emission by dissociative recombination leads to internal contradictions. We will now explore the consequences of the assumption that the dissociative recombination terms are negligible in Eqs. (1), (3), and (4). Strong evidence for this assumption is provided by recent studies of the helium afterglow.6 We shall see, furthermore, that the analysis then results in an agreement with the theory of collisional-radiative recombination so that an internal consistency is achieved. Mass spectrometer measurements in the afterglow would allow a more definitive discussion than the above.

With the dominant recombination mechanism now assumed to be that of collisional-radiative recombination, we expect little or no difference between the recombination coefficients, $\alpha(n)$ and $\alpha_M(n)$, of the atomic and the molecular ions. Under this assumption, we can rewrite Eqs. (1) through (5) using the definitions

$$y(t) \equiv \alpha(n)n(t), \qquad (12)$$

$$\Delta \equiv \delta [He]^2 = 110 p^2 \text{ at } 300^{\circ} \text{K},$$
 (13)

²¹ A. V. Phelps and J. P. Molnar, Phys. Rev. **89**, 1202 (1953). ²² E. C. Beaty and P. L. Patterson, Phys. Rev. **137**, A346 (1965).

²⁸ C. B. Collins, Phys. Rev. 140, A1850 (1965).

where p is the neutral gas pressure in Torr, and

$$\frac{\bar{D}}{\Lambda^2} = \frac{D}{\Lambda^2} \left[\text{He}^+ \right] + \frac{D_M}{\Lambda_M^2} \left[\text{He}_2^+ \right]. \tag{13a}$$

The equations then become

$$\frac{\dot{n}}{n} = -y - \frac{\bar{D}}{\Lambda^2} + \gamma \frac{[2^3 S]^2}{n},\tag{14}$$

$$\frac{d[\mathrm{He^+}]/dt}{[\mathrm{He^+}]} = -y - \frac{D}{\Lambda^2} - \Delta + \gamma \frac{[2^3 S]^2}{[\mathrm{He^+}]},$$
(15)

$$\frac{d[\mathrm{He_2}^+]/dt}{[\mathrm{He_2}^+]} = \Delta \frac{[\mathrm{He}^+]}{[\mathrm{He_2}^+]} - y - \frac{D_M}{\Lambda_M^2},$$
(16)

$$\frac{\dot{I}_A}{I_A} = \frac{\dot{y}}{y} + \frac{d[\text{He}^+]/dt}{[\text{He}^+]} = \frac{\dot{\alpha}}{\alpha} + \frac{\dot{n}}{n} + \frac{d[\text{He}^+]/dt}{[\text{He}^+]}, \quad (17)$$

and

$$\frac{\dot{I}_{M}}{I_{M}} = \frac{\dot{y}}{y} + \frac{d[\operatorname{He}_{2}^{+}]/dt}{[\operatorname{He}_{2}^{+}]}.$$
(18)

We have here neglected the term k_A/k_A in Eq. (17) and a similar one in Eq. (18) on the grounds that the dependence of k_A on time, through the electron temperature, is very slow.

Since a molecular band is also observed, we can obtain additional information by proceeding as follows. Equations (15) and (16) are substituted into the difference between Eqs. (17) and (18) to obtain

$$\frac{[\text{He}_2^+]}{n} = \frac{\Delta}{\dot{I}_M/I_M - \dot{I}_A/I_A + D_M/\Lambda_M^2 - D/\Lambda^2}.$$
 (19)

Where data were available to allow the use of this equation, typical values of $[\mathrm{He_2}^+]/n$ varied from 0.07 at 150 μ sec to 0.3 at 1.4 msec and 0.4 at 3 msec. The contribution of the diffusion terms is $\sim 100~\mathrm{sec^{-1}}$ and is therefore negligible in the early afterglow where $\dot{I}_M/I_M-\dot{I}_A/I_A\gtrsim 10^3$.

The recombination coefficient can be extracted in three different ways. First of all, the n(t) measurement is sufficient by itself to determine $\alpha(n)$ from Eqs. (12) and (14). There are two serious objections to this approach. We need prior knowledge as to the value of D/Λ^2 and, secondly, we require the determination of the time derivative of n, as a function of time, a rather inaccurate procedure.

A second approach is to use both the I(t) and n(t) data, thus obtaining $\alpha(n)$ from the equation

$$\alpha(n) = \frac{I(t)}{n^2(t)} \frac{y(t_0)n(t_0)}{I(t_0)}.$$
 (20)

We can in principle determine D/Λ^2 from the difference between n/n at two different times, preferably

widely separated. However, the exact value of D/Λ^2 so calculated will depend on which values of time are chosen. Furthermore, determining n/n from the available data for a time late in the afterglow is at best inaccurate.

A third and better approach, is to use the $I_A(t)$ measurement supplemented only by the values of n and n at a time t. We pick a value of D/Λ^2 which holds for some reference temperature. The function D/Λ^2 versus t is then determined if $T_e(t)$ is known, since D is proportional to the electron temperature. By the solution of two successive differential equations, we then determine y(t) and $\alpha(t)$. Using Eq. (12), n(t) is also calculated. This calculated n(t) curve is then compared with the experimentally determined one and the whole calculation is repeated for different values of D/Λ^2 until the best fit is found. In more detail, we proceed as follows. Substitute Eq. (15) into Eq. (17) thus obtaining the differential equation

$$\dot{y} - y^2 - yF(t) = 0$$
, (21)

where F(t) is the experimentally determined function

$$F(t) = \frac{\dot{I}_A}{I_A} + \frac{D}{\Lambda^2} + \Delta - \gamma \frac{\left[2^3 S\right]^2}{\left[\text{He}^+\right]}.$$
 (22)

The relative sizes of these terms for this experiment are $\gtrsim 10^3$: $\sim 200/p$: $110p^2$: $\lesssim 80$, where p is again the neutral gas pressure in Torr. The last term will now be neglected and the solution of Eq. (21) then becomes

$$y(t) = I_A(t) \exp \left[\int_{t_0}^t \frac{D}{\Lambda^2} dt + \Delta(t - t_0) \right] /$$

$$\left\{ \frac{I_A(t_0)}{y(t_0)} - \int_{t_0}^t I_A(t) \exp \left[\int_{t_0}^t \frac{D}{\Lambda^2} dt + \Delta(t - t_0) \right] dt \right\}. \quad (23)$$

The substitution of Eqs. (14) and (15) into Eq. (17) (last form) results in

$$\frac{\dot{\alpha}}{\alpha} = \frac{\dot{I}_A}{I_A} + 2y + 2 \frac{D}{\Lambda^2} + \Delta \,, \tag{24}$$

where we have again neglected the term in γ , and have assumed that $\bar{D}=D$. This assumption is very good when $[\mathrm{He_2}^+] \ll [\mathrm{He^+}]$, and will not lead to excessive error in the early afterglow even if $[\mathrm{He_2}^+] > [\mathrm{He^+}]$ since the diffusion terms are much smaller than other terms in Eqs. (14) and (15). Since y(t) is now known, we obtain as a solution of Eq. (24),

$$\alpha(t) = \frac{y(t_0)I_A(t)}{n(t_0)I_A(t_0)} \exp\left[2\int_{t_0}^t y(t)dt + 2\int_{t_0}^t \frac{D}{\Delta^2}dt + \Delta(t - t_0)\right]. \quad (25)$$

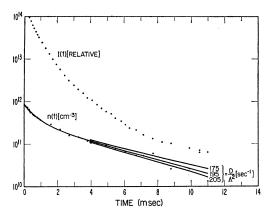


Fig. 4. Experimental 5876-Å light intensity and electron density as a function of time are indicated by dots. The lines are calculated n(t) curves and show the type of fit to experimental n(t) which is possible. Although this is an unusually good fit for very late times, all the data could be fitted well to calculated n(t) curves to at least 2 or 3 msec.

Finally, from Eq. (12),

$$n(t) = y(t)/\alpha(t). \tag{26}$$

The initial condition $y(t_0)$ is given by

$$y(t_0) = -\frac{\dot{n}(t_0)}{n(t_0)} - \frac{D}{\Lambda^2} \bigg|_{t_0} + \gamma \frac{[2^3 S]^2}{n} \bigg|_{t_0}, \tag{27}$$

where there is here somewhat less reason for neglecting the term in γ and also less inconvenience in keeping it.

The starting time for the calculation t_0 was always chosen so that the initial temperature and radial distribution variations which follow the discharge cutoff had already occurred and a new quasi-equilibrium had been reached. Typically, t_0 was chosen to be $100 \, \mu \text{sec}$ in the afterglow. An accurate calculation of $\dot{n}(t_0)/n(t_0)$ is greatly helped, at least in the present experiment, by the convenient fact that from $100 \, \mu \text{sec}$ to approximately 1 msec, the function 1/n(t) plots linearly against time. Thus $\dot{n}(t_0)/n(t_0) = -n(t_0) \times (\text{slope of the plot})$. Note that the slope of this plot does not equal the recombination coefficient, as was frequently assumed in earlier work.

To a first approximation in Eqs. (23) and (25) we can assume that D/Λ^2 is a constant, thus ignoring its dependence on the electron temperature. The value of D/Λ^2 then becomes the time average over the total interval being studied. Even in this approximation, agreement of calculated n(t) with experimentally measured n(t) to within experimental error can be obtained from $100 \, \mu \text{sec}$ to 11 msec in the afterglow. This agreement is shown in Fig. 4 for one set of data. The ratio $\alpha(n)/n$ is then plotted versus n in Fig. 5 superimposed on a family of curves representing predictions of the collisional-radiative recombination theory. Corresponding values of the measured electron temperature are indicated for certain times in the afterglow. Beyond

2 msec the electron temperature measurements become unreliable. It is reasonable however to expect a rapid decrease in the temperature in this region. This is consistent with the "tailing-off" of the experimental curves in Fig. 5. In comparing with the theory we should therefore consider only those parts of the curves which are earlier than 2 msec in the afterglow. With this in mind we see that the data exhibit generally good agreement with the theory of collisional-radiative recombination. At this point however, a still unanswered question is why the electron temperature remains elevated during a long period in the afterglow after falling abruptly by a factor of between 1.3 and 2 immediately following cutoff of the plasma current.

METASTABLE DENSITIES AND ENERGY BALANCE

Consideration of the continuity equation for the density of $\text{He}(2^3S)$ metastables in the light of its measured time dependence in the afterglow Fig. 6, forces us to include a term of the form $k^*n(t)$ corresponding to collisional de-excitation by electrons. Hence we write

$$\frac{d[2^{3}S]/dt}{[2^{3}S]} = \beta[2^{1}S]\frac{n(t)}{[2^{3}S]} + 0.75\frac{y(t)[\text{He}^{+}]}{[2^{3}S]} - \frac{D}{\Lambda^{2}} - \gamma[2^{3}S] - k[\text{He}]^{2} - k^{*}n(t). \quad (28)$$

The term in β is due to the reaction

$$\text{He}(2^{1}S) + e \xrightarrow{\beta} \text{He}(2^{3}S) + e + 0.79 \text{ eV},$$
 (29)

the next two terms are the contributions of recombination into triplet levels and diffusion respectively, the term in γ is due to loss by metastable-metastable colli-

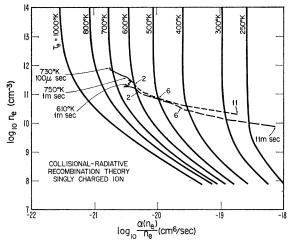


Fig. 5. Experimentally determined $\alpha(n)/n$ is plotted versus n for the He⁺ ion. Superimposed is a family of curves indicating the predictions of collisional-radiative recombination theory for a singly charged ion.

sions [Eq. (6)], and that in k to loss by the reaction

$$\text{He}(2^3S) + 2 \text{ He} \xrightarrow{k} \text{He}_2(2^3\Sigma_u^+) + \text{He}(1^1S).$$
 (30)

The factor 0.75 results from the statistical weights of the singlet and triplet levels. An experimental lower limit of 0.7 for this factor is provided by a direct measurement of the number of 5876-Å photons per recombination event.24 The singlet metastable density, determined from optical absorption of the 5016-Å line, is ~3×109 cm⁻³ in the early afterglow. It decays more rapidly than the triplet metastable density. Using the values $\beta = 3.5 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1} \text{ and } k = 2.5 \times 10^{-34} \text{ cm}^6$ sec⁻¹ given by Phelps,²⁵ we find that when Eq. (28) is solved for k^* we obtain a value of approximately 10⁻⁸ cm³ sec⁻¹. Assuming an electron temperature of 500°K, we then use $v = 1.2 \times 10^7$ cm sec⁻¹ in the equation $k^*=v\sigma$ and obtain a cross section $\sigma\sim 10^{-15}$ cm². This value is very approximate and is subject to possible error due to uncertainties in the true metastable density as detailed previously. The value of $\lceil 2^3 S \rceil$ used above may be too small and thus the values of k^* and σ , too large.

The cross section for the collisional de-excitation of $He(2^3S)$ by electrons has been calculated by Ferguson and Schluter²⁶ based on the measurements of Schulz and Fox²⁷ for the inverse reaction. They obtain a cross section of 8×10^{-17} cm² which is independent of electron temperature up to 3000°K. Considering the uncertainties inherent in evaluating the terms of Eq. (28) and especially in determining the absolute magnitude of $\lceil 2^3 S \rceil$, the order of magnitude between the two cross sections probably does not imply any basic disagreement with the value calculated by Ferguson and Schluter. Loss by collisions with He⁺ ions, with other 23S metastables, or with impurities, cannot, because of the lower densities and velocities of these particles, yield a term of the required magnitude without resorting to cross sections larger than 10^{-14} cm². It seems therefore that only de-excitation by electron collisions is adequate to explain the experimental observations. This conclusion would be changed only if the true triplet metastable density were more than a factor of 10 higher than the given values. This would in turn impose the very unlikely requirement that the 3^3D concentration be equal within 10% to the 2^3P concentration (see discussion in section on Experimental Procedure). Collisional deexcitation results in an electron of energy 19.8 eV, and is therefore also instrumental in maintaining the electron temperature during the afterglow.

Other possible mechanisms which can contribute energy to the electron gas are He(23S) metastable-

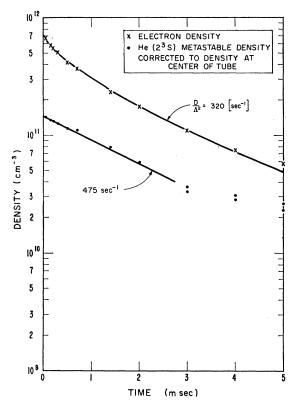


Fig. 6. Time dependence of 23S helium metastable density.

metastable collisions, which release electrons of about 9-eV average energy,28 transformation from 21S to 23S metastables by superelastic electron collisions releasing 0.79 eV and the collisional-radiative recombination process itself. In this latter process, an electron, newly attached to a positive ion in a very high level, gradually loses energy to free electrons until it reaches a level where radiative transitions downward become favored relative to collisional transitions.²⁹ For our conditions of electron density and electron temperature, this occurs at a level of principal quantum number 5 or 6, lying about 0.4 eV below the continuum. Thus for each recombination event, a quantity of energy $V_{\text{ion}}(n) \sim 0.4$ eV should be transferred to the electron gas. At a pressure of 1 Torr in a positive column afterglow, Ingraham and Brown²⁸ find that the major source of afterglow heating is that of metastable-metastable collisions, although at not very much lower pressures, collisional de-excitation does become dominant. This difference in dominant heating mechanism is thought to result from the very much lower ratio of $[2^3S]/n$ for the electron-beam excited, negative glow discharge used in the present experiment.

The differential equation describing the temperature

²⁴ E. E. Ferguson (private communication).

²⁵ A. V. Phelps, Phys. Rev. 99, 1307 (1955).

²⁶ E. E. Ferguson and H. Schluter, Planet. Space Sci. 9, 701 (1962).

²⁷ G. J. Schulz and R. E. Fox, Phys. Rev. 106, 1179 (1957).

²⁸ J. C. Ingraham and S. C. Brown, Phys. Rev. 138, A1015 (1965).

²⁹ S. Byron, R. C. Stabler, and P. I. Bortz, Phys. Rev. Letters 8, 376 (1962); 8, 497E (1962).

balance is

$$\frac{d}{dt}kT_{e} = -2\frac{m}{M}\nu_{m}(kT_{e} - kT_{g}) + \alpha(n)nV_{\text{ion}}(n)
+9\gamma \frac{[2^{3}S]^{2}}{n} + 19.8k*[2^{3}S] + 0.79\beta[2^{1}S]$$
(31)

in units of eV electron⁻¹ sec⁻¹. Here T_g is the temperature of the neutral gas, and ν_m is the electron-neutral collision frequency.³⁰

The time constants involved in this equation are all short ($\sim 10^{-6}$ to 10^{-5} sec) but it is known from the pulsed probe measurements that the electron temperature varies only rather slowly following its initial rapid drop. A quasi-equilibrium must therefore be reached and we may neglect the time derivative in Eq. (31). Defining the ratio $\Theta = T_e/T_g$ and using $\nu_m = 1.8 \times 10^8 \Theta^{1/2}$, one thus obtains

$$\Theta^{1/2}(\Theta - 1) = 0.78 \times 10^{-3} y(t) V_{\text{ion}}(n) + 0.84 \times 10^{-11} [2^{3}S]^{2}/n + 1.5 \times 10^{-10} [2^{3}S] + 2.2 \times 10^{-10} [2^{1}S]. \quad (32)$$

Using typical observed values of the metastable densities at $100 \,\mu\text{sec}$, $[2^3S] \cong 1 \times 10^{11} \,\text{cm}^{-3}$ and $[2^1S] \cong 3 \times 10^9 \,\text{cm}^{-3}$, it follows from Eq. (32) that if all the energy of the metastable-meststable and metastable-electron collisions were coupled efficiently to the electron gas, the electron temperature would be very high, above 2000°K . Consequently only a fraction of this energy must go into heating the electron gas, the remainder presumably being lost to the neutral gas.

The rate of recombination controls the metastable density in the afterglow to a large extent, and consequently all of the above heating processes are dependent, either directly or indirectly, on the recombination rate. For high electron densities, the collisional-radiative recombination rate is proportional to n^3 , therefore one might expect the rate of energy input per electron to increase rapidly as the electron density is raised above 10^{12} cm⁻³. If so, then it is clear that a helium plasma, in near equilibrium and of high electron density, must of necessity have an electron temperature several times room temperature, even during much of the afterglow.

RECOMBINATION OF THE He++ ION

Using the same experimental apparatus and measuring techniques described above, it has been possible to study the time dependence of the light intensity of the 4686 Å ($n=4\rightarrow n=3$ transition) of excited He⁺ during the afterglow. These measurements, together with measurements of electron density and electron temperature, allow a determination of the coefficient for

collisional-radiative recombination of electrons with doubly charged atomic helium ions. The analysis in this case is in many respects more simple than for the case of the recombination of singly charged atomic helium ions.

It was found that, if the duration of the discharge was sufficiently long (≈3 to 5 msec) that the plasma reached equilibrium, the 4686-Å line was then obscured by those lines in the P branch of the 4650-Å molecular helium rotational band which nearly coincide with it. Care was thus necessary in choosing the duration of the discharge for a given excitation current in order to maximize the light intensity of the 4686-Å line relative to the intensity of this rotational band. In order to accomplish this, it was found necessary to reduce the duration of the discharge to the neighborhood of 1 msec. The optimum duration for a given discharge current was fairly critical. For shorter durations the 4686-Å intensity dropped abruptly and for longer durations the 4650-Å intensity soon became too large.

Since the recombination coefficient of the He⁺⁺ ion is considerably higher than that of the He⁺ ion, the decay of the 4686-Å light is quite rapid and measurements were possible only over the range from 10 to $200\,\mu$ sec in the afterglow, a peak intensity being reached at approximately $30\,\mu$ sec. The measurable intensity range was as much as a full decade. During this same time interval, the intensity of the 4650-Å band increased, rising by as much a factor of 5 for the data taken at a pressure of 1.2 Torr. In the worst situation the 4650-Å band intensity amounted to no more than four or five times the 4686-Å line intensity and the two still appeared completely resolved. For the data at a pressure of 1.0 Torr the 4650-Å intensity was always much less than that of the 4686 Å.

Because of the short time scale involved, and because the He⁺⁺ ion is a very minor constituent of the plasma as a whole ([He⁺⁺] $\sim 10^8$ cm⁻³), the electron density remained almost constant, a typical change being <10% during the 200 μ sec interval of interest. This of course greatly simplifies the analysis. The differential equation governing the concentration of He⁺⁺ during the afterglow is

$$d[\text{He}^{++}]/dt = -\alpha^{+}(n)n[\text{He}^{++}]$$
$$-\frac{D}{\Lambda^{2}}[\text{He}^{++}] - \epsilon[\text{He}][\text{He}^{++}]. \quad (33)$$

Here $\alpha^+(n)$ is the coefficient for recombination of doubly charged atomic helium ions with electrons, written in two-body form but actually without any assumption concerning the mechanism involved since, as before, an arbitrary dependence on n is allowed. A diffusion loss term is next, followed by a term in ϵ which is the rate coefficient for the possible charge exchange reaction

$$\text{He}^{++} + \text{He} \xrightarrow{\epsilon} \text{He}^{+} + \text{He}^{+} + 29.8 \text{ eV}.$$
 (34)

³⁰ The predominant electron collisions are still those between electrons and neutral atoms. The frequency of electron-ion collisions is lower by a factor of 5 than that of electron-neutral collisions.

The equation for the intensity of the 4686-Å line is given by

$$I(\mathrm{He}^{+*}) = \mathrm{const}\alpha^{+}(n)n[\mathrm{He}^{++}]. \tag{35}$$

Taking the logarithmic derivative, we obtain

$$\frac{\dot{I}}{I} = +q \frac{\dot{n}}{n} + \frac{d[\text{He}^{++}]/dt}{[\text{He}^{++}]}.$$
 (36)

Here $\dot{\alpha}^+(n)/\alpha(n)$ is equated to $(q-1)\dot{n}/n$, where $1 \le q$ ≤ 2 . If collisional radiative recombination is dominant, then we expect the value q=2. Solving Eq. (33) for $\alpha^+(n)n$, we substitute Eq. (36) to eliminate $(d[He^{++}]/dt)/[He^{++}]$ and thus obtain

$$\alpha^{+}(n)n = -\frac{\dot{I}}{I} + 2\frac{\dot{n}}{n} - \frac{D}{\Lambda^{2}} - \epsilon [\text{He}]. \tag{37}$$

Because of the near constancy of the electron density one would expect the time dependence of the 4686-Å intensity to be essentially exponential. In confirmation, the experimentally measured decays can be fitted to exponentials having time constants between 36 and 122 usec, the precision of the time constant so determined being $\pm 10\%$. These values correspond to magnitudes of -I/I of the order of $10^4 \, \mathrm{sec^{-1}}$. Experimental values of $-\dot{n}/n$ are $\sim 300 \text{ sec}^{-1}$. The value of D/Λ^2 , higher by a factor of approximately³¹ 2 than the value for the singly ionized ion, is close to 500 sec⁻¹. Together, these last two terms modify the right-hand side of Eq. (37) by less than 10%.

It remains to consider the effect of the term ϵ [He]. We will consider this term to be significant if its value is $>300 \text{ sec}^{-1}$. Since [He] $\leq 3 \times 10^{16} \text{ cm}^{-3}$ this is equivalent to a value of $\epsilon > 10^{-14}$ cm³ sec⁻¹. The quantity ϵ is equal to $v\sigma$ where v is the thermal velocity of He⁺⁺ ions and is approximately equal to 1×10⁵ cm sec⁻¹. Therefore a cross section for charge exchange by reaction (34) in excess of $\sigma \sim 10^{-19}$ cm² would be significant.

The theory of nonsymmetric charge transfer reactions is quite complicated and the cross section in question cannot, at the present time, be predicted with any accuracy. The concept of adiabatic collisions³² is, however, useful in judging the significance of the charge transfer process. The adiabatic condition is achieved when the collision time L/v is very much greater than the electronic transition time $h/\Delta E$, where L is a distance over which the collision occurs, ΔE is the energy separation between initial and final states, and v is the relative velocity of approach. Most nonresonance charge transfer reactions therefore have negligibly low cross sections at thermal energies.

Exceptions to this rule can arise however in certain cases where there occurs a pseudocrossing of the initialand final-state potential-energy curves. In such a case

Table I. Measured recombination coefficients $\alpha^+(n)$ for doubly ionized helium with electrons at different electron densities and temperatures.

$\alpha^{+}(n) \text{ (cm}^{3} \text{ sec}^{-1})$	$n \text{ (cm}^{-3})$	T (°K)	P (Torr)
0.78×10^{-7} 0.57×10^{-7} 0.83×10^{-7} 0.64×10^{-7}	3.5×10^{11} 3.3×10^{11} 2.1×10^{11} 1.26×10^{11}	720 780 (heated) 660 630	1.2 1.2 1.0 1.0

the exact potential curves do not of course cross, 33 but do closely approach each other at the "crossing radius." Both ΔE and v must then be evaluated at the crossing radius and L becomes the extent of the region of close approach. Since ΔE will then be less than ΔE_{∞} , and v may be greater than the asymptotic initial velocity of approach, the adiabatic condition may not be satisfied at the crossing radius even when the asymptotic initial velocity is extremely small.

Geltman has calculated the potential energy curves of the initial state (He++He) and final state (He+ +He⁺) to first order using the complete electronic interaction.34 The curves (both of which are repulsive potentials) do not cross even in first order. Their energy separation varies only slowly with r and reaches a minimum separation of about 12 eV at 0.9 Bohr radii. The introduction of second-order polarization effects will modify the curves slightly but the minimum energy separation will still be approximately 12 eV and the relative velocity v will not be much above thermal. The adiabatic condition, $L\Delta E/hv\gg 1$, will then be satisfied for this reaction.

We therefore drop the term in ϵ from Eq. (37) and proceed with the calculation of the recombination coefficient. The measured values of $\alpha^+(n)$, n, T, and Pfor four separate measurements made at two different pressures and on two different days are shown in Table I. The second measurement listed is a repeat of the first with the electron temperature artificially raised by shining diathermy radiation (2450 MHz) onto the plasma. The corresponding values of $\alpha^+(n)/n$ are plotted versus n in Fig. 7 and are superimposed on curves which show the predictions of the collisional-radiative recombination theory for a doubly charged ion. These curves were calculated using a computer program developed at the National Bureau of Standards, Washington, D.C. and kindly made available by W. Wiese.

Comparison of the experimental points with these theoretical curves shows a systematic shift. Agreement can be forced by introducing either a factor of 2 in the values of $\alpha^+(n)/n$ or a shift of 10% in the values of the electron temperature. There is some recent evidence35 that the pulsed probe measurements may overestimate the temperature by just this amount. It must however

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22 E. W. McDaniel, Collision Phenomena in Ionized Gases (John

Wiley & Sons, Inc., New York, 1964), p. 240.

⁸³ G. Herzberg, Molecular Spectra and Molecular Structure Spectra of Diatomic Molecules, 2nd ed. (D. Van Nostrand, Inc., Princeton, New Jersey, 1950), p. 295.

³⁴ S. Geltman (private communication) ³⁵ R. S. Powers, J. Appl. Phys. **37**, 3821 (1966).

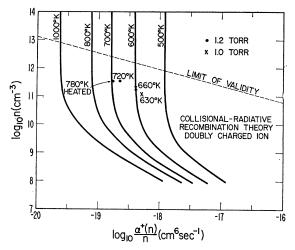


Fig. 7. Experimentally determined $\alpha^+(n)/n$ for the He⁺⁺ ion is plotted for several values of n and T_e . Superimposed is a family of curves indicating the predictions of collisional-radiative recombination theory for a doubly charged ion. The limit of validity indicated is discussed in Ref. 5.

be emphasized that uncertainties in the cross sections used in the theory of collisional-radiative recombination lead in any case to uncertainties of a factor of 2 in the value of $\alpha^+(n)/n$.

Referring to Fig. 7, we can see that the quantity $\alpha^+(n)/n$ should depend only very slightly if at all on n. A plot of $\alpha^+(n)/n$ versus the electron temperature then indicates a temperature dependence of $\alpha^+(n)/n$ to a power of approximately -5.

The experimental points are therefore in very good agreement with the theory of collisional-radiative recombination with respect to both the magnitude of the recombination coefficient and its temperature dependence.

SUMMARY

An analysis of spectral line intensity and electron density measurements as a function of time allows a determination of the coefficient for recombination of atomic ions with electrons. Simultaneous measurements of the electron temperature then permit a comparison with the theory of collisional-radiative recombination. Agreement is obtained to within a factor of approximately 2 in the value of $\alpha(n)/n$ or a factor of approximately 1.2 in the electron temperature.

The measured time dependence of the 2^3S metastable density in the continuity equation indicates that the dominant loss mechanism for 2^3S metastables is collisional de-excitation by electrons.

A study of the possible heating mechanisms suggests that the major mechanism in the early afterglow is that of de-excitation of the metastable atoms by electron collisions. Since all the heating mechanisms are controlled directly or indirectly by the recombination rate, it follows that the electron temperature in a helium afterglow must be elevated considerably above the neutral gas temperature until the electron density has dropped well below 10¹¹ cm⁻³.

In the case of the recombination of the He⁺⁺ ion, a more direct and less ambiguous analysis is possible. The experimental values are in very good agreement with the theory of collisional-radiative recombination and exhibit the predicted temperature dependence.

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