Electron Removal in Argon Afterglows*

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Ambipolar diffusion and recombination occurring in argon after the cut-off of a pulsed microwave discharge have been studied. The electron density and spectroscopic data obtained indicated that ambipolar diffusion is operative at low pressures, supplemented by recombination which is characterized by a relatively low recombination coefficient. At high pressures, electron removal is principally by recombination which is characterized by a relatively high value of recombination coefficient.

I. INTRODUCTION

ESSENTIALLY the same techniques as those described in the preceding paper[1] have been applied to the investigation of the various electron removal processes in argon afterglows. The reader is referred to this previous paper for a discussion of the method, definition of terms, etc.

The previous work bearing most directly on the present investigation[2] found a value of 3×10^{-7} cm^3/ion-sec for the recombination coefficient, α, between positive ions and electrons in argon. This value, along with those reported for several other gases, is considerably in excess of theoretical values[3] for direct radiative recombination. This fact makes detailed investigation of the *mechanism* of electron removal processes particularly important.

Earlier work[4] using probe techniques after the cut-off of a direct current discharge gave values of 2×10^{-10} cm^3/ion-sec for the recombination coefficient, but with low probable accuracy owing to a number of uncertainties in the measurements, the nature of which is discussed in the original paper. These measurements included a number of observations concerning the qualitative behavior of the spectrum of the afterglow as a function of time. As will be pointed out, many of these are in agreement with the present work. The recent work on the use of double probes rather than single ones for following plasma decays[5] makes it clear that it is necessary to be very careful in the interpretation of single-probe measurements after excitation has been removed.

II. HIGH PRESSURE MEASUREMENTS

In the pressure range above approximately 10 mm, electron removal from an argon plasma of moderate density (about 10^9 electrons/cm^3) is practically entirely by a recombination-type mechanism. The plots of $1/n$ *vs* t are very good, straight lines. With moderate power input to the microwave discharge (10 microsecond pulses, a few hundred-watts peak power), the recombination coefficient was found to be 1.1×10^{-6} cm^3/ion-sec independent of pressure over the range 20 to 30 mm.

In this same pressure range, an anomalous effect occurs with high input power (on the order of 1 kw peak). Two separate and distinct values of the recombination coefficient can be observed, depending on the excitation conditions, for the same sample of gas. This phenomenon is reproducible (at least with a spread of values on the order of ±15 percent), and gives values of 1.1×10^{-6} cm^3/ion-sec and 0.65×10^{-6} cm^3/ion-sec for moderate and high input power, respectively. The existence of these two distinct values for the recombination coefficient at short (250–600 microseconds) and long (greater than 1 millisecond) times in the same afterglow can be observed under proper excitation conditions; the electron decay curve (plotted as $1/n$ *vs* t) shows two straight portions separated by a curved transition region in this case. This effect has been observed only at the highest pressure studied (30 mm). It is thought that the existence of the lower value of the recombination coefficient associated with higher power excitation may be caused by the formation of a second type of ion (possibly a metastable; possibly a different molecular species) which recombines with its own characteristic coefficient. This explanation, although not entirely satisfactory, seems preferable, to us, to explanations based on variations of electron density across the discharge, etc. A similar effect has been noted in nitrogen.[6]

Our values should be compared with those of Biondi and Brown,[2] who obtained 0.3×10^{-6} cm^3/ion-sec. In general, these results certainly agree in order of magnitude with ours. Biondi and Brown expressed doubt, also, as to the purity of their argon. We took normal precautions in the preparation of our argon samples; spectroscopic observations of the discharge produced by microwave breakdown revealed only the singly ionized argon spectrum. Prolonged exposures with the discharge excited by a cw 2.5-mc oscillator showed traces of CO bands. In one bottle in which traces of nitrogen were detected, no differences as regards elec-

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[1] P. Dandurand and R. B. Holt, Phys. Rev. **82**, 868 (1951).
[2] M. A. Biondi and S. C. Brown, Phys. Rev. **76**, 1697 (1949).
[3] E. C. G. Stueckelberg and P. M. Morse, Phys. Rev. **36**, 16 (1930).
[4] C. Kenty, Phys. Rev. **32**, 624 (1928).
[5] E. O. Johnson and L. Malter, Phys. Rev. **80**, 58 (1950).
[6] R. Bryan, paper presented at the 1950 Conference on Gaseous Electronics.

tron removal were noted. Biondi and Brown used higher excitation power and longer breakdown pulses than we did. It should be pointed out that many of our measurements cover two orders of magnitude in time and in electron density, which gives us considerable confidence in the results.

Figure 1 shows a plot of light intensity (plotted as $1/I^{\frac{1}{2}}$ *vs* t) and electron density (plotted as $1/n$ *vs* t) data for a typical case. In all cases, the light intensity decay curve was found to approach an exponential behavior with a time constant of about 8 milliseconds at long times in the afterglow. This is owing to fluorescence of the quartz containers; this effect has also been noted in hydrogen afterglows.[7] Subtraction of the fluorescence background indicates that a two-body process is responsible for the radiation observed, since $1/I^{\frac{1}{2}}$ is then proportional to t. The fluorescence limited the range of observation, but the proportionality between light intensity and the square of electron density was found to be valid for a variety of pressures, ion densities, and excitation powers. Measurement of the total radiated energy in the visible and near ultraviolet spectrum gave an average value of 0.05 ev per electron removed; this indicates that a considerable number of the electrons are removed by radiative capture, but that this is probably not the primary process responsible for the electron density decay. These measurements, of course, apply only to the total intensity radiated. The qualitative changes in the spectrum as a function of various conditions will be discussed in a later section.

III. LOW PRESSURE MEASUREMENTS

Electron removal in the pressure range 0.5 to 1.5 mm agrees very well with amnipolar diffusion theory at low electron densities; plots of log$n$ *vs* t are good straight lines. A value of the product of ambipolar diffusion coefficient and pressure, $D_a p$, of 150 mm Hg·cm²/sec, corresponding to a value for the mobility, μ_0, of 1.4 cm²/volt sec (at 0°C, 760 mm), were obtained. These values were reproducible within ±10 percent. Recent work[8] has shown the existence of both atomic and molecular ions with differing mobilities in argon under certain conditions. Since we did not employ a mass spectrometer in this investigation, we are unable to state positively which type of ion the above measurements refer to; however, the spectroscopic data which we did obtain suggest that we were probably dealing largely with atomic ions.

In this pressure range, it is also possible to get a good estimate of the recombination coefficient by measuring the perturbing effect of recombination on electron-density decay due to ambipolar diffusion. The approximate equation under these conditions is

$$-dn_0/dt = 0.54\alpha n i^2 + D_a n_0/\Lambda^2,$$

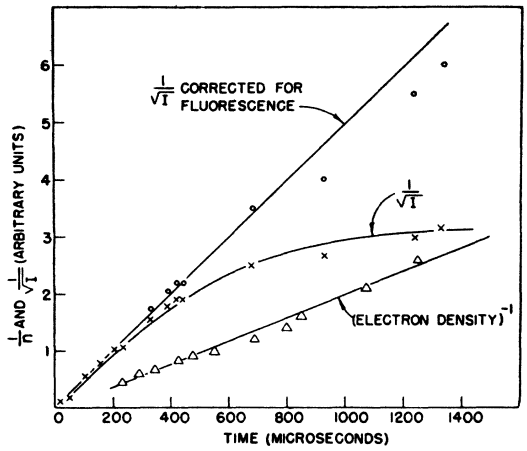

FIG. 1. Typical electron density and light intensity data at 20 mm pressure. Although not shown in this figure, the electron density data fall on the straight line out to 13 milliseconds.

where n_0 is the density of electrons at the center of a cylindrical container (with a bessel function radial and sinusoidal vertical distribution), and $1/\Lambda^2$ is $(\pi/h^2)+2.4/r^2$ (h is height, r is radius of container). This equation is derived in the Appendix. The exact solution of this equation is

$$n_0/(1+0.54\alpha\tau n_0) = \text{const} \times \exp(-t/\tau),$$

where τ is Λ^2/D_a. The recombination coefficient α is evaluated by choosing $\alpha\tau$ so as to obtain the best fit of the experimental data with the above equation. Data from a typical run is shown in Fig. 2. The actual treatment of the data involves plotting $n_0/(1+0.54\alpha\tau n_0)$ on a logarithmic scale *vs* t for several values of the parameter $\alpha\tau$, selecting the best straight line, and evaluating τ (and thus α) from the slope of this line. This method gives an average value of 4×10^{-8} cm³/ion-sec for α in this pressure range. This is considerably lower than the value obtained at higher pressure.

Evaluation of the recombination coefficient from electron removal data at intermediate pressures is difficult because of the competition of the two electron removal processes on an almost equal basis; however,

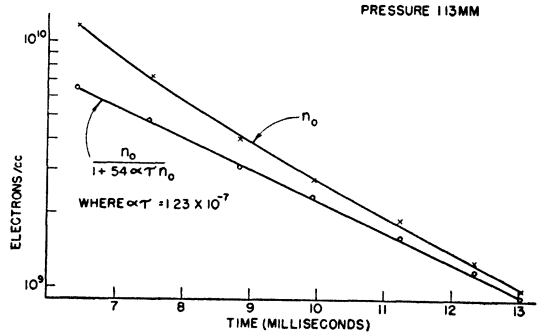

FIG. 2. Typical electron density data at low pressure, showing the method of estimating the recombination coefficient α.

[7] J. M. Richardson and R. B. Holt, Phys. Rev. **81**, 153 (1951).
[8] J. A. Hornbeck, Phys. Rev. **80**, 297 (1950).

we can set upper and lower limits for α which indicate that it has intermediate values at intermediate pressures.

Light intensity is proportional to the square of electron density under conditions where such measurements were feasible. Fluorescence background and low values of the recombination coefficient make observations difficult. The total radiated energy in the visible and near ultraviolet per electron removed *by recombination* is approximately the same as in the high pressure region.

Light intensity measurements, with high input power at times in the afterglow too short to permit simultaneous electron density measurements, show maxima at times of the order of 150 microseconds. A similar effect was noted by Kenty.[4] These maxima were not observed at low input power or at high pressures.

IV. SPECTROSCOPIC RESULTS

Analysis of the spectra obtained yields the following results (Paschen notation used): *In the visible*, at low pressures, the $2p-ms$ and $2p-md$ transitions are enhanced in the afterglow relative to the $1s-2p$ and $1s-3p$ transitions; also, the $1s-3p$ are enhanced relative to the $1s-2p$. This is in accord with Kenty's results;[4] he also reports that the higher term transitions within the $2p-ms$ and $2p-md$ are enhanced. Our data show only slight evidence of this enhancement; it is not so striking as in Kenty's experiment.

At higher pressures, the situation is reversed (!). The $1s-2p$ and $1s-3p$ transitions are definitely enhanced in the afterglow over the $2p-ms$ and mp transitions. Comparing the spectra during the discharge at different pressures, the $1s-2p$ and $1s-3p$ transitions are enhanced with increasing pressure.

Our data in the ultraviolet are incomplete. There seems, in general, to be little change in the spectrum between the discharge and the afterglow, although faint bands degraded to the ultraviolet with heads at about 3370 and 3578A were observed in the afterglow, in one case, at 18 mm pressure.

At high pressures, a continuum, in addition to a many-line spectrum, is observed during the discharge and in the afterglow, with no striking enhancement in the afterglow. This continuum contains an appreciable fraction of the total radiated energy.

V. CONCLUSIONS

At high pressures, electron removal in argon afterglows is principally by a recombination-type mechanism. Total light intensity measurements indicate that while radiative type capture probably plays some part in the removal, it is probably not the principal effect operative. Detailed analysis of the spectra observed does not suggest to us any very definite conclusions concerning the mechanism of either the radiative or the nonradiative part of this removal.

At low pressures, ambipolar diffusion is operative, supplemented by recombination which is characterized by a coefficient considerably smaller than that obtained at higher pressures. The spectrum emitted shows some qualitative difference from that at high pressures, but does not lead us to any definite conclusions regarding the explanation for the observed difference in recombination coefficients.

APPENDIX

The exact equation governing the electron removal process is

$$(-\partial n/\partial t)=\alpha n^2+D_a\nabla^2 n, \tag{1}$$

where n is the electron density as a function of space and time, and α and D_a are defined above. The boundary conditions are that $n=0$ on the surface of the container, which is cylindrical. This equation and boundary conditions cannot easily be solved exactly or by a straightforward perturbation method in α.

If α equals zero, the solution to the equation is a sum of cylindrical harmonics with different exponential decays in time. We make our measurements at a time long enough in the afterglow so that the high order solutions have decayed and we have essentially a first-order distribution:

$$n=n_0\sin(\pi z/h)J_0(2.4r/R), \tag{2}$$

where $n_0=\text{const}\times\exp(-t/\tau)$, and τ is defined above.

When α is dufficiently large to perturb the solution, the approximation we make is to assume that the spatial distribution of the electrons is the same as in the unperturbed case. Then substituting Eq. (2) into Eq. (1) and integrating over the volume of the container, we get

$$(-dn_0/dt)=0.54\alpha n_0^2+(n_0/\tau).$$

We feel that this approximation is somewhat preferable to that of Biondi and Brown,[2] who assume that the recombination process behaves as if the distribution were uniform, with a density equal to the average density of the unperturbed distribution. This approximation gives

$$(-dn_0/dt)=0.27\alpha n_0^2+(n_0/\tau).$$