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RECOMBINATION IN THE AFTERGLOW OF A MERCURY DISCHARGE

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ABSTRACT

A mercury-arc discharge through a 500-cm³ bulb is extinguished by short-circuiting two anodes on each side of the bulb by a commutator, and probe measurements are made at varying time intervals after the cutoff. Most of the measurements are limited to discharges of 6 and 4 amperes at a vapor pressure of 270 μ. Probe measurements of the number of ions per cubic centimeter in the bulb and of the ion current to the bulb wall give the number of ions recombining in the space and the recombination coefficient 2.3×10^{-10}. The electron temperature decreases with time from 3,000° K at 10^{-3} sec to 1,600 at 6×10^{-3} sec. Theoretical considerations indicate that this is probably not a spontaneous two-body recombination.

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I. INTRODUCTION

Another paper[1] reports experiments on the rate of recombination of ions and electrons in the afterglow of a cesium discharge. The method was to measure the number of ions per cubic centimeter at different time intervals after cutting off the discharge and also to measure the flow of ions to the walls. From these data one can derive the number of ions which recombine in the space and the recombination coefficient, α defined by the equation

$$dn/dt = -\alpha n^2, \tag{1}$$

where n is the number of ions or electrons per cubic centimeter. A value of $\alpha = 3.4\times10^{-10}$ was found at pressures ranging from 10 to 33 μ and an electron temperature of about 1,200° K.

It is of interest to obtain comparable measurements in other elements. The only other published value for this coefficient under low-pressure discharge conditions is an estimate obtained by Kenty [2] of 2×10^{-10} for ions in the afterglow of an argon discharge. He estimates an uncertainty of fivefold in this result and, in view of this, it remains of interest to see whether different elements have comparable values of α at low pressure. Experiments by Webb and Sinclair on the

[1] Fred L. Mohler. J. Research NBS 19, 447 (1937) RP1036.
[2] Kenty. Phys. Rev. 32, 624 (1928).

radiation emitted by a jet of vapor from a mercury discharge [3] add interest to the project for they reach conclusions that seem quite incompatible with some of the cesium results. Using the intensity of the visible spectrum as a measure of recombination, they conclude that the rate of recombination increases as the first power of the electron concentration and decreases very rapidly and exponentially with increasing electron temperature.

II. METHOD

A mercury-cathode arc was used for the discharge, and as this cannot be interrupted and restarted by a simple circuit, the device was used of having two anodes on each side of a 500-cm³ bulb, which

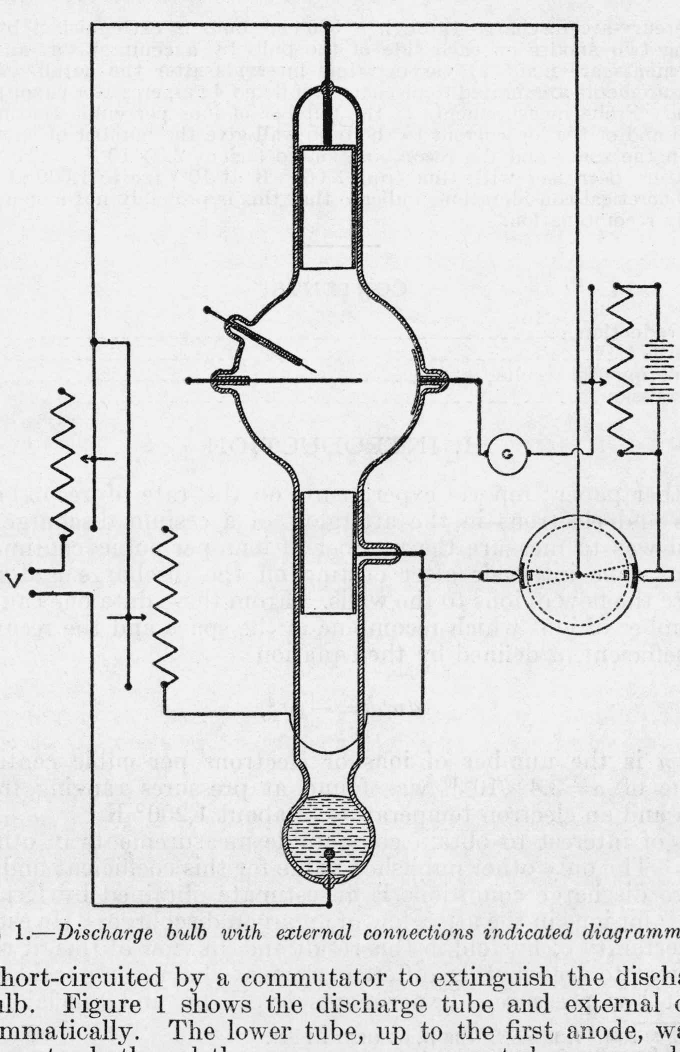

FIGURE 1.—*Discharge bulb with external connections indicated diagrammatically.*

were short-circuited by a commutator to extinguish the discharge in the bulb. Figure 1 shows the discharge tube and external circuits diagrammatically. The lower tube, up to the first anode, was in a stirred water bath and the vapor pressures quoted correspond to the

[3] *Recombination in mercury vapor.* Phys. Rev. **37,** 182 (1931).

temperatures of the bath. Actually, a somewhat higher vapor pressure was probably maintained by the arc. At a pressure of a few microns of mercury the glow extends well above the lower anode when the two anodes are short-circuited. At higher pressures this is not noticeable and check measurements show that the fast electrons diffusing into the space are quite negligible in comparison with the currents obtained when the commutator is running. There is a potential drop of 1 or 2 volts across the commutator brush when the commutator is closed. This has been compensated by a low-resistance potential divider (not shown in the diagram). If it is not compensated, and the potential of the upper anode is slightly positive, then the probe currents in the afterglow period are larger and the recombination coefficient somewhat smaller. This effect has been discussed by Hayner[4] and Kenty.[5]

The motor-driven commutator short-circuits the discharge for about 0.004 sec twice in a revolution at full speed. A second commutator throws one of the three probes into the circuit for 0.001 or 0.002 sec at an adjustable interval after the discharge is cut off. The motor was run at about 1,200 and 600 rpm.

The flow of ions to the wall was measured by a disk electrode 3 cm in diameter. A small positive probe of 4-mil wire 0.5 cm long measured electron concentration by the conventional method. As the precision of this measurement was rather low, a second method was also used. The positive current to a large negative probe was measured and by comparison with the small positive probe the proportionality factor between ion current and ion concentration was found. The time change in ion concentration was obtained with better precision from the change in positive current.

III. EXPERIMENTAL RESULTS

In the interpretation of the probe measurements it is assumed that the ion current density measured by the disk is characteristic of the entire bulb wall and that the ion concentration as measured by the probes is typical of the entire volume. In the case of the cesium afterglow, stroboscopic observations indicated that this was a fair approximation, but such observations have not yet been made with the mercury afterglow.

Figure 2 gives three groups of current-voltage curves for the three probes at different time intervals after cutting off a 6-ampere discharge in mercury vapor at 270 μ pressure. The group at the lower right gives the positive-ion current to the disk. The slope at negative voltages comes from a capacity effect which approaches zero at the wall potential, so that a linear extrapolation to the wall potential gives the flow of ions to an insulated surface. The group of curves at the left shows the positive current to the large probe. The slope at negative voltages is here largely accounted for by the area of the space-charge sheath. This area is equal to the area of the wire at the space potential and this potential has been obtained from the current-voltage curve of the small probe. The ion current at the space potential has been computed from the measured current at various negative potentials by means of the space-charge equations for cylindrical

[4] Hayner. Z. Phys. **35**, 365 (1925).
[5] Kenty. Phys. Rev. **32**, 624 (1928).

collectors.[6] The upper curves show the electron current to the small probe on a semilogarithmic scale. The applied potentials have been corrected for the voltage drop across the microammeter. Since the instantaneous voltage drop is 25 times that for an equal steady current this correction becomes very important. The curves show the two

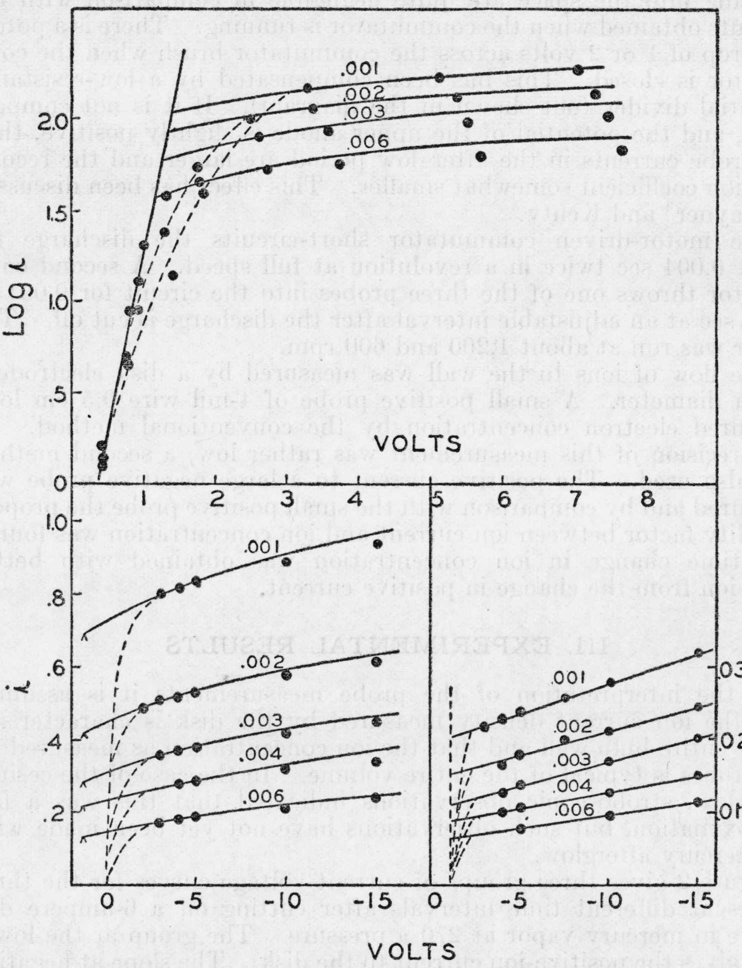

FIGURE 2.—*Current-voltage curves for the three probes.*

Numbers on the curves indicate time in seconds after the cutoff. Above, semilog plot of electron current to small positive probe; lower left, positive current to large probe; lower right, positive current to disk.

characteristic branches at potentials negative and positive with respect to the space potential, while close to the space potential there is a rounding off of the observed points, which, for small time intervals, extends over several volts. At longer intervals there is very little rounding off, and the results compare favorably with the best probe measurements under static conditions.

The slope of the branch on the left gives the electron temperature but with low precision, because the curve is very steep. This tem-

[6] Langmuir and Blodgett. Phys. Rev. 22, 347 (1923).

perature drops with increasing time (the separate curves could not be shown on the scale of fig. 2). A representative series of measurements of electron temperature is shown in table 1, and for comparison, figures read from a published curve of Randall and Webb for a jet of mercury streaming from an arc at 390 μ. The two methods are entirely concordant. The temperature in the discharge is about 8,000° K.

TABLE 1.—*Electron temperatures in an afterglow at a pressure of 270 μ and in a jet at 390 μ*

Time	Afterglow (4-amperes discharge)	Jet[1]
Seconds	°K	°K
0.001	2,960	3,000
.002	2,270	2,500
.003	2,020	2,000
.004	1,900	1,900
.006	1,600	1,600

[1] Randall and Webb. Phys. Rev. **48**, 544 (1935).

The right branches of the upper curves can be accounted for, as in the case of the negative probe, by the area of the space-charge sheath, and the same method was used to find the current density.

Electron concentration was derived from the current density by the relation,

$$n_e = 4.03 \times 10^{13} i_e / T_e^{\frac{1}{2}}, \tag{2}$$

where T_e is the electron temperature. The ratio of n_e to the current density of positive ions, as measured by the large probe, was found for each set of measurements and the mean value, excluding measurements at 0.001 sec, was

$$n_e = 1.18 \times 10^{15} i_+ \tag{3}$$

There is an uncertainty of about 10 percent in individual measurements, while at 0.001 sec the ratio is less and the error greater. The evidence is that this error is largely in the electron-current measurements. It is of interest that this constant is nearly equal to the rate at which ions would diffuse to the probe by thermal agitation at a temperature equal to the gas temperature. Taking this temperature as 400° K, the equation for positive ions analogous to eq 2 gives,

$$n_e = 1.22 \times 10^{15} i_+$$

This is not a relation that could be assumed a priori, for at lower pressures pure diffusion does not account for the currents.[7] It seems probable that the ion temperature, unlike the electron temperature, will drop almost instantly to the gas temperature and that the coefficient in eq 3 will remain nearly constant over the range of time intervals used.

The rate of change of the total number of ions in the bulb is assumed to be equal to the rate at which they flow to the walls, plus the rate at which they recombine in free space.

$$\Delta N / \Delta t = A i_+ / e + V \alpha n_e^2, \tag{4}$$

[7] Tonks and Langmuir. Phys. Rev. **34**, 876 (1929).

where A is the area of the walls, i_+/e the number of ions flowing to the walls per square centimeter per second, V is the volume of the bulb, and n_e the number of electrons or ions per cubic centimeter. In practice Δt is far from infinitesimal and mean values of i and n_e over the interval Δt are used.

Figure 3 includes all measurements at 270 μ made with currents of 6 and 4 amperes. Curve *I* gives the rate of change of the total number

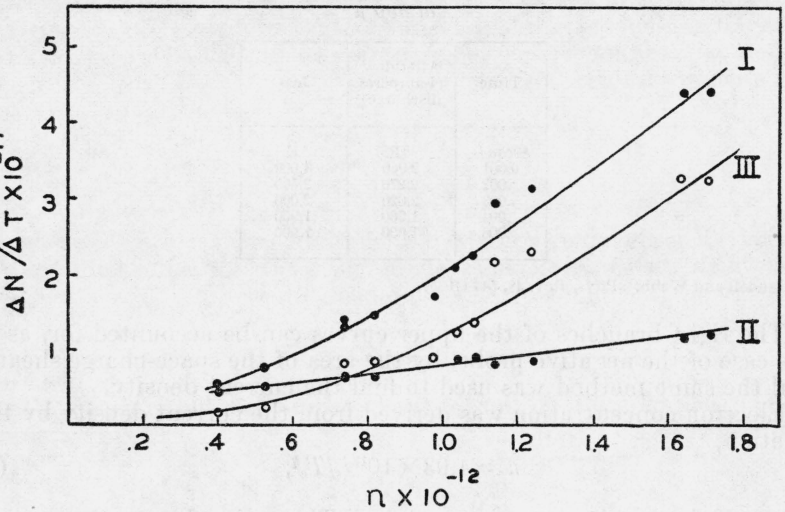

FIGURE 3.—*$\Delta N/\Delta t$ as a function of the mean electron concentration over the time Δt.*

Curve *I* shows the decrease in total number of electrons in the bulb; *II*, the flow of ions to the wall; and *III*, the volume recombination.

of ions as a function of the mean value of n_e, curve *II* is the rate of flow of ions to the walls, and curve *III*, the difference between *I* and *II*, is the number recombining in the space per second. Curve *III* has been drawn proportional to n_e^2 and, with two exceptions, it fits the observations within the range of experimental uncertainty. This curve gives the value $\alpha = 2.3 \times 10^{-10}$, and the mean error of the 10 measurements is 0.4×10^{-10}. Measurements at lower pressures give comparable values but with much greater uncertainty, and it is doubtful whether they have any significance. The procedure of maintaining a discharge in the side tube during the afterglow may vitiate the low-pressure results.

IV. DISCUSSION

The value of the recombination coefficient of mercury ions, 2.3×10^{-10}, pertains to an electron temperature of about 2,000° K and a pressure of 270 μ. This is to be compared with the experimental result for cesium of 3.4×10^{-10} at an electron temperature of about 1,200° K and pressures between 10 and 30 μ. The value reported by Kenty for argon ions at a pressure of 800 μ is not significantly different from either of these. It is of interest that the values for common gases as measured near atmospheric pressure would give a similar magnitude of about 5×10^{-10} at 300 μ, on the assumption that α is proportional to the pressure. This may be entirely accidental as quite different processes seem to be involved. In the afterglow free electrons recombine, while at higher pressures electron attachment to form negative ions probably precedes recombination.

The question as to whether the low-pressure recombination coefficients pertain to spontaneous two-body recombination involves theoretical uncertainties indicated by the following considerations.

The recombination of hydrogen ions into various quantum levels has been evaluated for two approximations. For the case in which the kinetic energy of the electron is small compared to the energy of the quantized level, the recombination coefficient α_n for levels of total quantum number n can be expressed [8]

$$\alpha_n = 5.94 \times 10^{-13} A_n V^{-1/2} \tag{5}$$

$$A_n = 0.326/n \text{ for } n=3 \text{ or more,}$$

where V is the energy of the electron in electron volts. For the case in which the kinetic energy of the electron is much greater than the energy of the quantized level, Oppenheimer [9] gives a relation which can be expressed

$$\alpha_n = 6.3 \times 10^{-11}/V^2 n^3 \tag{6}$$

The recombination coefficient for electrons of kinetic energy V is the sum of α_n for all values of n. Equation 5 can be used for values of n less than n_0, where

$$n_0 = (13.54/V)^{1/2}, \tag{7}$$

while eq 6 is valid for values of n much greater than n_0. As a rough approximation, one can apply eq 5 and 6 to all values of n which are respectively less or greater than n_0. For $V=0.1$ volt n_0 falls between 11 and 12. From eq 5 and published values of A_n

$$\sum_{1}^{11} \alpha_n = 1.7 \times 10^{-12} \tag{8}$$

From eq 6 and 7 and the approximation $\sum_{n_0}^{\infty} n^{-3} = \frac{n_0^2}{2}$

$$\sum_{n_0}^{\infty} \alpha_n = \frac{6.3 \times 10^{-11}}{V^2} \sum_{n_0}^{\infty} \frac{1}{n^3} = \frac{2.3 \times 10^{-12}}{V} \tag{9}$$

For 0.1-volt electrons eq 6 gives 2.3×10^{-11} for the contribution of all levels with n greater than 12. Large errors are introduced by assuming that eq 6 is valid from n_0 to $2n_0$, but the summation is certainly greater than one-fourth of the above value. The contribution of all levels with n less than n_0 is negligible, and eq 6 alone can be used to compute the recombination coefficient. As levels of large n and l values are

[8] Stueckelberg and Morse. Phys. Rev. **36**, 16 (1930), give values for all n and l states to $n=5$, and the author has evaluated their equations for $n=5$ and $n=6$.

[9] Oppenheimer. Phys. Rev. **31**, 349 (1928).

predominant all singly charged ions will be very similar to hydrogen and it is probably permissible to apply the hydrogen equations to mercury and cesium ions. However, serious physical limitations in testing the theory arise from the fact that energy levels of high n values are important. Under laboratory conditions of pressure and ion concentrations, such levels are greatly perturbed.

In spite of the theoretical uncertainties, it seems fairly certain that the experimental values of 2 or 3×10^{-10} cannot be considered as coefficients of spontaneous recombination and that at pressures as low as 10 μ in cesium the effect of pressure is to enhance the probability of recombination. It is evident that atomic and electronic collisions will also have an opposite effect of ionizing excited states, so that what is here called recombination is more accurately the difference between the rate of recombination and the rate at which ions are created in the afterglow. This ionization of highly excited states is exactly the type of process postulated by Webb and Sinclair to explain the rapid decrease in recombination radiation with increasing electron temperature.[10] This work gives no evidence of any large change in the recombination coefficient as the mean electron temperature changes from 2,800 to 1,800° K for curve *III* of figure 3 would not change as n_e^2 if this were the case. The conditions of measurement and the quantities measured are entirely different in the two experiments, so that the results are not necessarily contradictory. It is important to measure the recombination coefficient over a wide range of conditions, but the type of discharge tube used here is not well adapted to the purpose.

WASHINGTON, August 10, 1937.

[10] Webb and Sinclair. Phys. Rev. 37, 182 (1931).