

## RECOMBINATION IN MERCURY VAPOR

BY HAROLD W. WEBB\* AND DAVID SINCLAIR

PHYSICS LABORATORIES, COLUMBIA UNIVERSITY, NEW YORK CITY

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## ABSTRACT

The afterglow in ionized mercury vapor was studied as a recombination phenomenon, to determine how its intensity varied with concentration of electrons and of positive ions, vapor pressure and the mean energy of the electrons, the last expressed as a temperature,  $T$ . The afterglow was observed in a region outside of the arc to which positive ions and electrons were carried by a stream of vapor, auxiliary electrodes being used to control the electron temperatures. The total number of electrons,  $N$ , was assumed closely equal to the number of positive ions. The intensity of the visible part of the afterglow radiation was shown to be closely proportional to the total intensity under the experimental conditions, and was therefore used as a measure of the rate of recombination. This intensity,  $I$ , was found to be proportional to the first power instead of to the square of the electron concentration, with possible exceptions at low concentrations and low electron temperatures.  $I$  varied with vapor pressure, increasing roughly as the fourth power of the pressure. With increase in electron temperature from  $1300^\circ$  to  $5600^\circ\text{K}$ ,  $I$  decreased by a factor of 2500. From this rapid change in  $I$  it is concluded that the afterglow cannot be due to a simple recombination process, since work of other authors with caesium and helium has shown that  $I$  should then vary not more rapidly than the reciprocal of the temperature. The results were found to fit either of the following empirical equations:  $I = \text{const } N^2/N_0$  or  $I = \text{const } N^2/N_1$ , where  $N_0$  is the number of fast electrons having energies greater than a determined value and  $N_1$  the number having a definite energy. The values of the critical energies corresponding to these two equations were found to be 1.15 volts and 1.35 volts, respectively.

The results suggest that the recombination in mercury vapor takes place in two stages, of which the second is responsible for the radiation of the series lines, and that the effect of the fast electrons is to reionize from the first stage.

Considerable difficulty was experienced during measurements as the result of changes in the contact potential of the exploring electrodes used for measuring electron temperatures and concentrations. These changes were apparently due to traces of oxygen.

THE recombination of ions and free electrons has been studied in various ways but the nature of the process is still very obscure. The results of these studies have been well summarized in several recent publications,<sup>1</sup> and only a few outstanding points need be reviewed here. Especially have the simple recombination of an ion and an electron accompanied by emission of radiation and the converse process of photoionization been investigated in detail. The most extensive quantitative experiments in this field have been

\* The appointment of the senior author as Ernest Kempton Adams Fellow enabled him to secure the collaboration of Mr. Sinclair.

<sup>1</sup> Seeliger *Phys. Zeits.* **30**, 329 (1929); Mohler, *Phys. Rev. Supp.* **1**, 216 (1929); Compton and Langmuir, *Rev. of Mod. Phys.* **2**, 191 (1930).

made by Mohler,<sup>2</sup> who found in caesium vapor and in helium continuous spectra extending from near the series limits to higher frequencies. These spectra are interpreted as due to the recombination of ions with electrons, in which process an electron falls into the lowest energy level of one of the series, the difference in frequency between that of the radiation observed,  $\nu$ , and that corresponding to the series limit,  $\nu_i$ , being due to the kinetic energy of the electron before impact,  $mv^2/2$ . The relation between these frequencies is given by  $h\nu = h\nu_i + \frac{1}{2}mv^2$ . In these experiments the mean energy of the electrons was about 0.3 volt. Mohler found that the intensity of the radiation varied as a function of the electron velocity,  $v$ , and determined the value of the coefficient of recombination;  $\alpha = \text{const. } v/(\nu - \nu_i)v^2$ , or  $\alpha$  is proportional to  $1/vv^2$ . Theoretical studies<sup>3</sup> of the process give  $\alpha$  proportional to  $1/v$ ,  $1/vv$ , or similar expressions in fair agreement with experiment. It is of particular interest to note that, in these experiments, the rate of recombination of electrons and positive ions was found to vary very slowly with the kinetic energy of the electrons, that is inversely as the first power of the velocity, in marked contrast with results to be described later.

Hayner<sup>4</sup> has shown that the afterglow in mercury vapor is due to some process of the nature of recombination. In her experiments the voltage on a low-voltage arc in mercury vapor was abruptly cut off and the behavior of the radiation which persisted, called the "afterglow," studied in the post-arc period immediately thereafter. The cutting off of the arc voltage extinguished the spectral series lines practically instantaneously, but after a brief transition period of about  $10^{-4}$  sec. the series lines reappeared gradually increasing in intensity, reaching a maximum in about  $2 \times 10^{-4}$  sec. and then gradually decreasing. The behavior of the ionized gas in the experimental tube in the post-arc period gave every evidence that the afterglow was the result of a recombination process involving electrons and positive ions. The dark transition period following the cut-off of the arc voltage was explained as due to the fact that the velocities of the electrons were too great to permit recombination. The subsequent gradual growth of the intensities of the series lines corresponded to the gradual decrease in these velocities due to impacts with neutral atoms, while the decrease following the maximum was the result of the disappearance of ions and electrons due to their recombination and to diffusion to the walls of the tube. The nature of the spectrum of the afterglow furnishes additional evidence that it is produced by a recombination process. In it the ratio of the intensities of the higher members of the spectral series to the intensities of the lower members is very much greater than in spectra resulting from direct impact excitation as are observed in the arc.

Kenty<sup>5</sup> in a similar experiment in argon found like results. The mean energy of the electrons at the time when the afterglow was most intense in the

<sup>2</sup> Mohler, *Phys. Rev.* **31**, 187 (1928); Mohler and Boeckner, *B. S. J. of Res.* **2**, 489, **3**, 303 (1929).

<sup>3</sup> Seeliger, reference 1, p. 356.

<sup>4</sup> Hayner, *Zeits. f. Physik* **35**, 365 (1926).

<sup>5</sup> Kenty, *Phys. Rev.* **32**, 624 (1928).

post-arc period was determined by the Langmuir probe method as 0.4 volt, confirming the explanation that the recombination in the arc period and in the dark transition period was prevented by the high speed of the electrons and that radiation from recombination only became observable after the electrons had lost most of their energy.

Measurements on gases highly ionized, subject to no impressed field, have in general shown that the distribution of velocities among the electrons is Maxwellian and that a definite "temperature" may be assigned to the distribution. The Langmuir probe method gives a means of determining this temperature and gives also data for computing the concentrations of ions and electrons. The fact that the electrons have such a distribution, or one nearly approaching it, makes it very difficult to reconcile Hayner's results with the theory that the observed afterglow was due to simple recombination of positive ions and electrons, in which the probability of electrons of given velocity recombining with positive ions depends only upon the concentration and velocity of those electrons and the concentration of the ions. For, as we have seen, the most effective electrons in recombination are the slow ones. Now the number of these in a Maxwellian distribution varies with the temperature approximately as  $1/T^{3/2}$ , the total number being kept constant. Now on liberal estimates the total change in the electron temperature from the transition period, when the intensity of the afterglow was too small to observe to the moment of maximum intensity, was in Hayner's experiment not greater than a ten-fold decrease; on the other hand the change in intensity during this time appears to have been of a different order of magnitude, estimated as at least a thousand-fold increase. The intensity could not therefore have varied as the number of electrons moving slowly enough to have high probability of recombination, unless the velocity distribution was not Maxwellian but one in which the slower electrons were relatively very much scarcer at the higher temperatures. There is every evidence that this was not the case. Considerations of this difficulty in interpreting these results lead to the experiments described in this paper, in which the intensity of the afterglow was studied as a function of electron temperature, concentrations of positive ions and electrons and vapor pressure.

#### APPARATUS AND METHOD

To avoid the difficulties of making precise determinations of electron temperatures and concentrations under the rapidly changing conditions in the "post-arc" period following the cut-off of an arc, the investigations of the afterglow were made in a region outside the arc to which the positive ions and electrons were carried by a stream of vapor. The apparatus used was similar to that described in an earlier paper.<sup>7</sup> The essential parts of the experimental tube, drawn to scale, are shown in Fig. 1. The mercury in the pool below the cathode *K*, was heated by a furnace, *H*, and the vapor streamed rapidly past

<sup>6</sup> Rayleigh, Proc. Roy. Soc. **A108**, 262 (1925).

<sup>7</sup> Webb and Wang, Phys. Rev. **33**, 329 (1929).

the cathode and the anode, *A*, into the branch tube through the gauze, *G*, past the observation point, *P*, and was condensed in the region marked *C*. The cathode was an internally heated nickel cylinder with oxide coating.\* The gauze, *G*, was of nickel wire, 0.03 cm in diameter and 0.6 cm spacing. At *P*, in the center of the tube, was placed a vertical probe, consisting usually of a platinum wire 0.0025 cm diameter exposed for about 0.5 cm. Opposite the probe was a quartz window 1.2 cm in diameter attached by a graded seal. A side tube 0.7 cm in diameter and 7 cm long closed at the end extended out at right angles near *P*, and was used in estimating the vapor pressure in the tube at this point. The condenser, *C*, was cooled by a coil of lead tubing carrying circulating water. This coil could be adjusted as to length and position

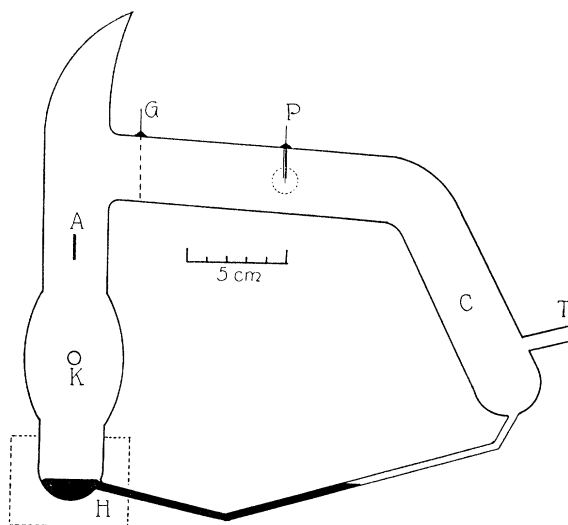


Fig. 1. Diagram of experimental tube.

or replaced by air cooling to control the flow of mercury vapor in the tube. Premature condensation in the tube between the furnace and the condenser was prevented by secondary heaters.

The pumping tube, *T*, passed first to a McLeod gauge, then to a magnetically operated cut-off and finally to a mercury diffusion pump. During observations this pump was in constant operation.

The arc current was varied up to 10 amperes, with an average potential drop of about 8 volts. From below the anode was emitted the usual low-voltage arc radiation with the higher members of the series relatively weak in intensity, while beginning a little above the anode and extending throughout the branch tube and the condenser was the afterglow in which the higher members of the series were relatively much stronger. The intensity of the

\* For this cathode we are indebted to Mr. L. J. Buttolph of the General Electric Vapor Lamp Co.

afterglow at the point  $P$  was measured by a specially constructed visual photometer sighted through the quartz window. The radiation thus measured was practically all contributed by the sharp triplet  $\lambda\lambda 5461, 4358, 4047$ , and the intensities of these lines were taken as a measure of the total radiation of the afterglow. To justify this assumption spectrograms of the glow at different electron temperatures were made and compared and it was found that at least up to the 11  $D$  and 7  $S$  members the ratios of the intensities of the above triplet to those of the higher members varied only slightly, not sufficiently to introduce serious error. Rayleigh<sup>6</sup> reports considerable variation in these ratios with age of the afterglow, but presumably the conditions in the present investigation were not so widely varied as in his. Furthermore, as will be seen later, small errors resulting from this method of measuring the intensity of the afterglow would not have affected appreciably the nature of the results.

Simultaneously with the intensity measurements observations were taken with the probe to determine the corresponding concentration of the electrons and their temperature. It was assumed that the number of positive ions was practically equal to that of the electrons, which for concentrations of the order observed is probably closely true. The usual logarithm of current to probe vs. probe-voltage plot gave, after deducting the current due to the positive ions, a straight line for voltages below the space potential, the slope of which determined the electron temperature. The concentration of electrons was computed from the space potential, as determined by the break in the curve, and the probe dimensions in the usual way. It should be noted that under the conditions of this experiment the distribution of electron velocities could be followed only up to about 0.7 volt (in a few cases to 1.0 volt) owing to the masking by the positive ions of the electron currents to the probe at greater negative potentials. Therefore the presence of the fast electrons is indicated only by the fact that the Maxwellian distribution holds very closely for the slow electrons and we assume it to hold for higher speeds.

Considerable difficulty was experienced with the probe owing to changes in its contact difference of potential in the course of a measurement. This was evidenced by a gradual shift in the voltage corresponding to a given current to the probe. The curve taken with increasing voltage did not coincide with that for decreasing voltage. The direction and amount of the drift were not always the same but depended upon the material used for the probe, its size and the presence of small amounts of impurities in the tube. In general one to two minutes were required for any phase of the change. When, however, the currents to the probe were large the resultant heating caused more rapid changes. A complete discussion of the many tests made cannot be given here, but it may be noted that similar effects were found with platinum, tungsten, iron and carbon probes; a tungsten probe continuously heated to a temperature of about 1700° C was equally unsteady; a trace of sodium accidentally introduced into the tube resulted in a characteristic fluctuation.

It is probable that this drift was due to traces of oxygen in the tube. To test this an artificial leak was introduced near the cathode, as the result of

which the changes in the contact potential of the probe became very rapid, confirming this conclusion. It was further found that, although all metal parts were pre-outgassed and the tube baked at 500° C for many hours before introducing the mercury, considerable gas was evolved when the arc was running even after many hours of operation. Tests, made by closing the cut-off and measuring the rate of accumulation of gas in the gauge, indicated that there was a gas pressure in the stream of mercury vapor of about  $10^{-7}$  mm at the times when marked drifting occurred. This drifting was never wholly eliminated, but, by continued baking and pumping, conditions were attained under which the drifting was sufficiently small to permit satisfactory measurements.

It is probable that many of the troubles experienced by other observers were due to this cause. The difficulty which Mohler and Boeckner<sup>8</sup> found with a probe in caesium vapor is not surprising, especially the increased unsteadiness when approaching large values of the probe current. It was found also in our work, as in theirs, that a large probe gave less trouble, since it suffered less rise of temperature. Other authors have obtained curves deviating from the expected straight line, or curves which are interpreted as made up of several straight lines indicating several groups of electrons each having a different temperature. Some of these complexities may have been due to effects similar to those described here.

The vapor pressure in the tube at the point of observation depended upon the temperature of the lower furnace and upon the use and position of the cooling coils on the condenser. The magnitude of this pressure was determined approximately by measuring the temperature at which liquid mercury was in equilibrium with the vapor at the end of the small side tube opposite the point of observation.

The electron temperature at the point of observation, though it depended to some extent upon the vapor pressure and the velocity of the vapor streaming from the region of the arc, was usually controlled by the gauze *G*. A positive potential on *G*, with respect to the anode, accelerated the electrons in the vapor stream and increased the temperature of those passing through the gauze and down the tube. Temperatures ranging from 1000° to 6000° could be obtained. The application of the positive potential to the gauze also decreased the concentration of the ions and electrons, in some cases as much as 70 percent. The concentration could, however, be brought back to its original value by increasing the arc current.

## RESULTS

In determining the relation between the intensity of the afterglow, *I*, and the electron temperature, *T*, the vapor pressure was held constant for each series of measurements. It was assumed that the only other variable was the concentration of the electrons, which was equal to that of the ions, and this was kept as nearly constant as possible by adjusting the arc current. As this

<sup>8</sup> Mohler and Boeckner, B. S. J. of Res. 2, 489 (1929).

concentration could be held only approximately constant the relation between intensity and concentration,  $N$ , was determined by a series of measurements in which the vapor pressure and electron temperature were kept constant. The results of these determinations are shown in Figure 2, in which the intensity of the afterglow is plotted as a function of the electron concentration. Three typical curves are shown, the differences in the slopes having no significance. These curves show that the intensity is closely proportional to the first power of the electron concentration, and not to the square of this concentration as might be expected if ordinary recombination processes were in question. Therefore, before studying the relation between intensity and

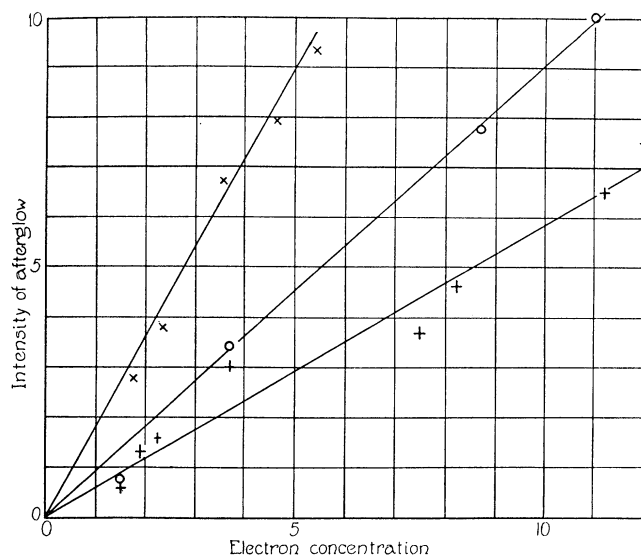


Fig. 2. Intensity of afterglow vs. electron concentration; electron temperature and vapor pressure constant. Scales are arbitrary.

electron temperature the intensities observed were divided by the first power of the corresponding number of electrons. Furthermore throughout any set of measurements of the relation of  $I$  to  $T$  the variation in  $N$  was not large and since the variation of the intensity with electron temperature was very rapid, errors arising from small departures from the first power relation were well within the limits of measurement.

It is interesting to note that Mohler and Boeckner<sup>8</sup> found a similar result with caesium. Contrary to expectation the intensity varied more nearly as the first power than as the square of the concentration of electrons, which was again equal to the number of positive ions. They noted, however, that at low currents the square law held. In the present experiment, also, there was indication that, for small concentrations especially at low electron temperatures, the square law more nearly described the results than the first power law. These results were however, not very dependable.

The relation between the intensity of the afterglow and the vapor pressure, the temperature of the electrons and the number of ions and electrons being held constant, was not precisely determined, owing to experimental difficulties. The results showed, however, a large increase in intensity with increase of vapor pressure. To a rough approximation the intensity varied as the fourth power of the vapor pressure within the limited pressure range observed, 0.06 to 0.10 mm. It is interesting to note that Mohler and Boeckner found in the recombination spectrum of caesium that the intensity increased surprisingly rapidly with vapor pressure, the rate of increase being comparable with that found in the present work.

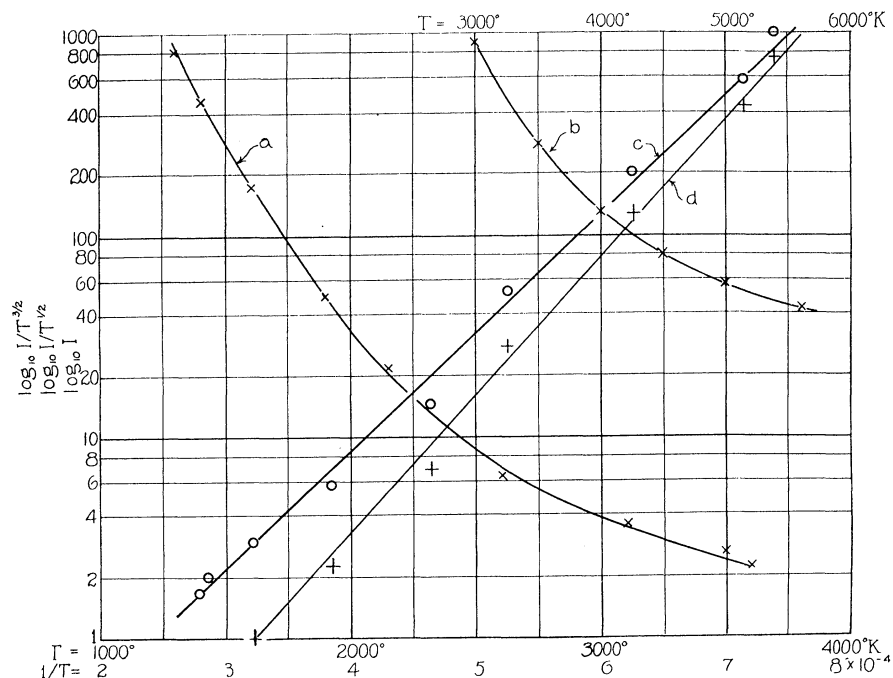


Fig. 3. Intensity of afterglow as a function of electron temperature; vapor pressure and electron concentration constant. Curve a:  $\log I$  vs.  $T$  (lower temperature scale). Curve b:  $\log I$  vs.  $T$  (upper temperature scale). Curve c:  $\log I/T^{1/2}$  vs.  $1/T$ . Curve d:  $\log I/T^{3/2}$  vs.  $1/T$ .

The experimental results giving the relation between the intensity of the afterglow,  $I$ , and the electron temperature are shown in Figure 3. Curve (a) shows the results for a vapor pressure of 0.06 mm. The ordinates are the intensities, corrected for variations in  $N$ , plotted for convenience as  $\log_{10} I$ . The abscissas are electron temperatures in  $^{\circ}\text{K}$ . In these measurements  $N$  was of the order of  $10^{11}$  per cc.

Curve (b) Figure 3, shows the results for another set of measurements at approximately the same vapor pressure. Owing to the fact that in this case no determinations of  $N$  were made, this curve has not been corrected to  $N =$



constant. The variation of  $N$  over this curve may have been as great as three-fold. The intensity scale is furthermore not the same as in Curve (a), owing to the use of a different photometric standard. This curve shows, however, that at higher temperatures the variation of  $I$  with  $T$  follows roughly the same law as in the lower temperature range. The striking feature of these curves is the very large decrease in  $I$  with small relative increase in temperature. Curve (a) shows a decrease in  $I$  of about 400 times as  $T$  increases from  $1300^\circ$  to  $3600^\circ\text{K}$ . Including the data of Curve (b) we see a decrease in  $I$  of about 2500 times as  $T$  changes from  $1300^\circ$  to  $5600^\circ$ .

#### DISCUSSION

As pointed out earlier the rapid change of intensity,  $I$ , with electron temperature,  $T$ , observed in the afterglow cannot be explained by any simple process of recombination in which the decrease in the rate of recombination depends simply upon the increase in the average velocity of all the electrons. For, if the recombination is similar to that observed in caesium, with the coefficient of recombination approximately proportional to  $1/v$  ( $v$  = electron velocity) and the electrons have a Maxwellian velocity distribution as seems to be the case, to a first approximation  $I$  should be proportional to the integral taken over all velocities of the number having a velocity  $v$  divided by  $v$ . This is equal to  $\text{const } N^2/T^{3/2}$  where  $N$  is the total number of electrons, considered here as held constant. The total change in  $1/T^{3/2}$  over the entire range of electron temperatures measured was not greater than 3, while  $I$  changed by a factor of nearly 2500, a different order of magnitude. Now, on the other hand, if we consider  $N_0$ , the number of electrons having energies greater than some given value,  $E_0$ , we see that this can be made to vary with the electron temperature as rapidly as we please, by proper choice of  $E_0$ . We have

$$N_0 = N \left[ \text{erf} (E_0/kT)^{1/2} + (2/\pi^{1/2})(E_0/kT)^{1/2} e^{-E_0/kT} \right]$$

in which expression, if  $E_0$  is not too small, the second term containing the exponential factor is the controlling one. (In the present work neglecting the first term introduces only an inappreciable error.) Now the simplest empirical relation between  $I$  and  $T$  which fits the results was found to be  $I = C_1 T^n e^{C_2/T}$ , equation (1), where  $C_1$  and  $C_2$  are constants and  $n$  is small. Because of the large value of the exponent the exponential term was found to be the important factor in determining the form of the curve and the precision of the measurements was not sufficient to enable one to differentiate between small values of  $n$ . The agreement between experiment and equation (1) can be seen from Curve (c), Figure 3, in which the data of Curve (a) have been replotted, with ordinates  $\log_{10}(I/T^{3/2})$  and abscissas  $1/T$ . The points fall well within the experimental error on the straight line,  $\log_{10}(I/T^{3/2}) = \text{const}/T + \log_{10} C_1$ . In this plot  $n$  was taken as  $\frac{1}{2}$  for reasons to be given below. Other series of measurements, taken at vapor pressures ranging from 0.06 mm to 0.10 mm when plotted in the same way gave nearly equally good agreement with the equation.

Now if  $I$  be taken proportional to  $N$ , as was found to be approximately true, equation (1), after rearranging, becomes:

$$I = \text{const } N^2 \div [N(2/\pi^{1/2})(E_0/kT)^{1/2}e^{-E_0/kT}] = \text{const } N^2 \div N_0 \quad (2),$$

where  $k$  is Boltzmann's constant. Thus we may express our results very well in the simple form, that the intensity of the afterglow varies directly as the square of the total number of electrons and inversely as the number of electrons having energies greater than  $E_0$ . If instead of  $N_0$ , we consider the number,  $N_1$ , of electrons having an energy equal to  $E_0$ , we arrive at a similar result.  $N_1$  varies as  $(1/T^{3/2})e^{-E_0/kT}$ , and if in equation (1) we put  $n = 3/2$ , we obtain the result,  $I = \text{const } N^2/N_1$ . This results in a linear relation between  $\log_{10}(I/T^{3/2})$  and  $1/T$ , as shown in Curve (d) Figure 3, in which the data of Curve (a) are expressed in these coordinates. We therefore find that we are in equally good agreement with experiment if in equation (2) we substitute  $N_1$  for  $N_0$ , which gives the result that the intensity is inversely proportional to the number of electrons having their energy equal to  $E_0$ . The part played by the fast electrons is thus to prevent the afterglow, the effect of electron temperature on the intensity depending primarily upon the change in the number of such electrons. It should be remarked that this general conclusion does not rest solely on the close fit of the results with the relations given above but seems to be a necessary conclusion from the observed rapid change of  $I$  with  $T$ , so long as we assume that the effect of each electron on the process is a function of its energy and not of the mean energy of the whole group of electrons.

The value of  $E_0$  as determined from the data of Curve (c) is 1.15 volt, from Curve (d) 1.35 volt. The values found from other series of measurements, when computed as in the case of Curve (c), range from 0.95 to 1.20 volt. The lowest value was obtained from a set of measurements covering only the lower temperatures and was probably affected by the fact that the intensities were often found to be less than those corresponding to the above equations when the electron temperature was below 1400°. Considering the precision of the measurements it seems probable that  $E_0$  is a constant, independent of the vapor pressure and other conditions and that the best average of the values determined is 1.15 volt when computed assuming  $I$  to depend upon  $N_0$ , and 1.35 volt if it depends upon  $N_1$ . Furthermore, unless the efficiency of this preventative action of the fast electrons rises very rapidly as their energies approach the value  $E_0$  from below, it seems that we must assume that  $E_0$  is a minimum or a critical value for the energy of an electron which can so function and not an average value.

There has been found no evidence that metastable or excited atoms of the  $2^3P$  states play any major part in the afterglow phenomenon.

Our results suggest that we are dealing with a process more complex than that of a simple recombination in which only a single electron and an ion take part, possibly a recombination process involving two electrons and an ion. The form of equation (2) suggests that this process is of the type illustrated by the following hypothetical picture, suggested by Mr. George Dean.

Assume that under the conditions in question complete recombination is accomplished in two stages, a first stage in which a slow electron falls into an outer level of the positive ion, and a second stage in which the electron makes a transition from this outer level to a lower level with the emission of series line radiation.\* The first stage may be assumed to be accompanied by continuous radiation and to be governed by the laws similar to those governing the recombination observed in caesium and helium discussed above. Assume further that fast electrons having energies greater than a certain minimum value  $E_0$  (or electrons having exactly the energy  $E_0$ ) to be capable of reionizing the atom which has experienced only the first stage of recombination. Let  $N'$  be the concentration of such "partially recombined" atoms. The rate of formation of these atoms is  $AN^2f(T)$  where  $Af(T)$  is the coefficient of recombination,  $A$  being constant. The rate at which these atoms would change into normal atoms is given by  $RN'$ , where  $R$  is a transition probability. The rate of reionization of the partially recombined atoms would be  $CN'N_0$ , where  $N_0$  is, as above, the concentration of electrons having energies in excess of  $E_0$ . Now we are observing a steady state in the vapor stream and  $N'$  is constant. If we neglect a small term giving the diffusion rate of  $N'$  into the space observed, we get

$$AN^2f(T) - RN' - CN'N_0 = 0 \quad (3)$$

or

$$N' = AN^2f(T)/(R + CN_0). \quad (4)$$

Now except for the smaller values of  $T$ ,  $R$  may be neglected with respect to  $CN_0$  in the denominator of equation (4), since for larger values of  $T$ ,  $RN'$  is negligible with respect to  $AN^2f(T)$  and therefore with respect to  $CN'N_0$ . This follows since  $RN'$  is proportional to the intensity of the afterglow,  $I$ , which decreases very rapidly with increase in temperature while  $AN^2f(T)$  varies not faster than  $1/T^{3/2}$ .

If  $f(T)$  is taken equal to a constant we have from (4)  $I = \text{const } N^2/N_0$ , agreeing with the empirical equation (2) which expresses the experimental results. If  $f(T)$  is taken equal to  $1/T^{1/2}$ , as suggested in the first paragraph of this section, we have  $I = \text{const } (1/T^{1/2})(N^2/N_0)$  which gives equally good agreement with experiment. The value of  $E_0$  in this case is about 7 percent lower than in the case of  $f(T) = \text{constant}$ .

In the above  $N_1$ , the number of electrons having exactly the energy  $E_0$ , may be substituted for  $N_0$  without further change except that the corresponding values of  $E_0$  would be increased by about 15 percent.

For the smaller values of  $T$  at which observations were taken and for small values of  $N$ ,  $R$  may be no longer negligible with respect to  $CN_0$  and we should then find the intensity less than would be expected from equation (2), and would further find for diminishing  $N$  that the intensity would vary more

\* Compare this with the "initial recombination" postulated by J. Franck (Zeit. f. Physik **47**, 509 (1928)): see also L. R. Maxwell (Phys. Rev. **32**, 715 (1928)).

nearly as the second power of  $N$ . The experimental results give evidence that this is the case, but are not sufficiently reliable to test this in detail.

It is obvious that the first stage of recombination assumed above may not necessarily involve an electron and a positive ion but may be the formation of some kind of molecular state, which in breaking up leaves the atom with such excitation as is necessary for the radiation of the arc lines. Recent studies by Mohler and Boeckner<sup>9</sup> of the photoionization of caesium indicate that the molecule ion plays a major part in that process and it is therefore probable that it is also an important factor in recombination. The picture given above represents only the type of process which the experimental results seem to indicate as necessary to account for the properties of the after-glow radiation in mercury vapor.

Lawrence<sup>10</sup> and other investigators have found a series of ultra-ionization potentials lying above the normal 10.4 volts ionization potential. The first four of these lie 0.20, 0.89, 1.30 and 1.66 volt, respectively, above 10.4 volts. It is suggested that the critical potential  $E_0$  may be related to one of these ionization potentials.

<sup>9</sup> Boeckner, B. S. J. of Res. **5**, 13 (1930); Mohler and Boeckner, B. S. J. of Res. **5**, 51, 399, 831 (1930).

<sup>10</sup> Lawrence, Phys. Rev. **28**, 947 (1926); Jarvis, Phys. Rev. **27**, 808 (1926); Hughes and Van Atta, Phys. Rev. **36**, 214 (1930).