obtained by the method of least squares using the doublet intervals in the third band where Coon considered his measurements to be most accurate. This gave $(\Delta\lambda/hc)=0.057$ cm^{-1}; $(\Delta\mu/hc)=0.0038$ cm^{-1}; $(\Delta\eta/hc)=0.0001$ to 0.0002 cm^{-1}. The constant $\Delta\eta$ is minute as one might anticipate from the fact that it is proportional to b and to $(\beta/B-\alpha/A)$, both of which vanish when the molecule has an axis of symmetry. Indeed, the results would not be altered appreciably if the term containing $\Delta\eta$ were omitted, that is, if the asymmetry of the molecule were disregarded entirely. It should be stated, however, that this term, tiny as it is, yet acts uniformly in such a direction as to improve the agreement between theory and experiment.

FINE STRUCTURE RESULTING FROM COUPLING OF NUCLEAR SPINS

There seems to be no reason why precisely similar results should not also apply when $S=0$ and nuclear spin holds the center of interest. An attempt to use them in describing fine structure observed in the inversion spectrum of $N^{14}H_3$ [19] has now been superseded by the excellent work of Gunther-Mohr.[4]

ACKNOWLEDGMENTS

My best thanks are due Professor J. H. Van Vleck under whose direction this work was done and whose ideas form the basis of it.

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Electron Loss Process in the Hydrogen Afterglow*

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Electron loss processes in the afterglow of very pure hydrogen have been studied by the microwave technique. The conclusion is drawn that within the error of the experiment, no electron-ion recombination is observed, and that high-mode diffusion is very evident. By properly accounting for the high diffusion modes, the results are given as $D_ap=700\pm50$ cm^2-mm Hg sec^{-1} with the electron-ion recombination less than 3×10^{-8} cm^{-3} sec^{-1}.

ELECTRON loss processes in the hydrogen afterglow have been studied by the microwave method by a number of workers. Although the results are related, no agreement has been achieved up to the present time as to the actual loss processes in hydrogen.[1–3] In view of the result of the work presented here, it is possible to understand the disagreement between the previous investigations of the hydrogen loss processes. The main result is that, if sufficiently pure hydrogen is used, the loss process for the electrons in the ranges covered by previous investigators, as well as by us, is explained by an ambipolar diffusion mechanism. If the electron-ion recombination is present, this loss process is so small that it cannot be measured with methods available at present.

MICROWAVE METHOD

The microwave method measures the frequency shift, Δf, of a resonant cavity containing the electron-ion plasma, relative to the resonant frequency, f, of the same cavity without the plasma. The relation between the frequency shift and the average electron density, $\langle n\rangle$, is

$$\frac{\Delta f}{f}=\frac{1}{2}\frac{1}{1+(\nu_m/\omega)^2}\frac{\langle n\rangle}{n_p},\tag{1}$$

where the average electron density $\langle n\rangle$ is given by

$$\langle n\rangle=\int_V nE^2dv\bigg/\int_V E^2dv.\tag{2}$$

The quantity $n_p=\epsilon_0 m\omega^2/e^2$, E is the electric field of the probing microwave signal, ν_m is the momentum transfer collision frequency per electron (ν_m is proportional to the pressure), ω is the applied radian frequency of the probing signal, and V is the volume of the microwave cavity. The linear relationship between the frequency shift and the average electron density holds only as long as the polarization field in the plasma is small compared with the applied microwave field. The error in linearity is less than 1 percent if $n\leq3\times10^8[1+(\nu_m/\omega)^2]$ cm^{-3}.

To interpret the measurements of the microwave method, it is necessary to recognize the fact that only an average electron density is measured. Neglecting the influence of the shape of the microwave field, the microwave method measures the total number of the

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[1] M. A. Biondi and S. C. Brown, Phys. Rev. 76, 1697 (1949).

[2] J. M. Richardson and R. B. Holt, Phys. Rev. 81, 153 (1951).

[3] L. J. Varnerin, Jr., Phys. Rev. 84, 563 (1951).

free electrons present in the cavity. Therefore, whatever the loss process is, the rate of loss of electrons refers to the total number of the electrons present. For a proper interpretation of the measurements it is necessary to know the electron density distribution. The three-dimensional electron density distribution, as well as the probing microwave mode, can be split into one symmetric and one antisymmetric part for each dimension. The microwave method using a symmetric mode measures only the symmetric part of the electron density distribution.

AMBIPOLAR DIFFUSION

We restrict our discussion to those times when the electrons can be considered in thermal equilibrium with the gas and when the space-charge-influenced diffusion is the dominant loss mechanism. The decay of the electron and ion densities is governed by the following equations:

$$\mathbf{\Gamma}_- = -D_-\nabla n_- - \mu_-\mathbf{E}m_-,\ \mathbf{\Gamma}_+ = -D_+\nabla n_+ + \mu_+\mathbf{E}n_+,$$
$$\partial n_-/\partial t + \nabla\cdot\mathbf{\Gamma}_- = 0;\ \partial n/\partial t + \nabla\cdot\mathbf{\Gamma}_+ = 0,$$
$$\nabla\cdot\mathbf{E} = e(n_+ - n_-)/\epsilon_0. \qquad (3)$$

Here $\mathbf{\Gamma}$ is the particle current density, D is the diffusion coefficient, μ the mobility; the subscripts indicate positive ions and electrons. A convenient system of proper variables for this equation system is: $t/p\Lambda^2$, x/Λ, n/Λ^2, $p\Lambda^3\mathbf{\Gamma}$, and $E\Lambda$, where Λ is the fundamental diffusion length. The solution to this equation system can be written in the general form $n\Lambda^2 = f[(\mathbf{r}/\Lambda), (t/p\Lambda^2)]$, where $\mathbf{r} = f(x,y,z)$. Unfortunately this function is not separable in terms of the variables $\mathbf{r}/\Lambda$ and $t/p\Lambda^2$. Since the microwave method measures an average electron density the averaging process has to be applied to these equations. The general result can be written in the form $\Lambda^2\langle n\rangle = g(t/p\Lambda^2)$. This solution is rigorous when the ion and the electron temperatures are independent of the coordinates. This form of the solution is also independent of the magnitude of the space charge. The function, g, depends upon the shape of the probing microwave field and the initial spatial distribution.

In the ambipolar limit, the equation system (2) may be reduced to the following equation which governs the decay of both the electron and the ion densities

$$\partial n/\partial t = D_a\nabla^2 n. \qquad (4)$$

The criterion for ambipolar diffusion described by Eq. (4) is $n > n_+ - n_- \approx \epsilon_0(kT/e^2\Lambda^2)$. The diffusion length used in this experiment was of the order of one centimeter, and at room temperature this criterion can be written as $n > 10^5$ cm^3.

In the experiment to be described, the gas is contained in a cubical quartz bottle placed at the center of the microwave resonator. The general solution for the average electron density in the ambipolar limit is simple to derive but lengthy to write down. For the one-dimensional case the general solution of the electron spatial density distribution can be written as

$$n\sum_i A_i \exp[(i\pi/L)^2 D_a t]\cos(i\pi x/L),$$
$$i = 1,3,5,7,\cdots. \qquad (5)$$

The first term of this series is the fundamental diffusion mode and the higher terms are therefore properly called higher diffusion modes. In the one-dimensional case, the ratios between the time constant for the decay of the fundamental mode and the higher modes are so large (the minimum ratio is 9) that it is customary to neglect the higher modes. In the three-dimensional case, the general solution consists of the product of three series like (4). The time constant for the fundamental diffusion mode is $T_1 = L^2/3\pi^2 D_a$, where L is the side of the quartz bottle. The ratios between this time constant and those of the higher diffusion modes are

$$T_1/T_2 = 3.67;\ T_1/T_3 = 6.33;\ T_1/T_4 = 9.$$

Since these ratios are relatively small, and the amount of higher diffusion modes present may be large, these higher diffusion modes may be present to a measurable extent rather late in the postdischarge period. The initial electron spatial distribution may vary widely and it becomes impossible to recognize the ambipolar diffusion process from the time dependence of the decay curve alone. The characteristic feature of the ordinary diffusion process, as well as of the space-charge-influenced diffusion, is that by using the proper time variable $t/p\Lambda^2$, the time dependence of the average electron density becomes independent of the pressure p, the fundamental diffusion length Λ, and the absolute value of the average electron density $\langle n\rangle$, for any given initial spatial electron distribution.

ELECTRON ATTACHMENT SUPERIMPOSED ON AMBIPOLAR DIFFUSION

The difficult feature of experiments of this kind is the problem of purity of the gas. The most serious impurities are those that form negative ions; they are oxygen and water vapor. The probability that an electron will attach to one of these molecules at room temperature is around 10^{-3}. In the ambipolar diffusion range and when attachment is present, the decay of the electron density is governed by the differential equation

$$\partial n/\partial t = D_a\nabla^2 n - hkNn. \qquad (6)$$

In the pure gas, the number of hydrogen atoms present is very small and we neglect the formation of negative hydrogen ions. The number density, N, is therefore the number density of the impurities; h is the corresponding probability for attachment; kN is the rate of collisions per electron with the impurities.

Assuming that the impurity desnity is so large that variations in N caused by the formation of negative ions can be neglected, the solution for average electron density takes the form

$$\langle n\rangle = K e^{-hkNt} g(D_a t/\Lambda^2), \tag{7}$$

where $g(D_a t/\Lambda^2)$ is the solution with no impurities present. Later in the afterglow when the higher diffusion modes have decreased to a negligible value relative to the fundamental diffusion mode, the average electron density becomes

$$\langle n\rangle = K \exp\{-[hkN + (D_a p/p\Lambda^2)]t\}. \tag{8}$$

Attachment losses are thus dominant in the late afterglow when $hkN \gg D_a p/p\Lambda$. The $(D_a p)$ for hydrogen, as measured in this experiment, is 700 cm^2 — mm Hg/sec; $\Lambda^2 = 1$ cm^2. The collision frequency between electrons and the impurities can be estimated to be of the order of $10^{10}\ p_i$/sec, where p_i is the partial pressure of the impurities. The criterion for dominant attachment losses can then be written $p_i/p \gg 10^{-4}/p^2$, where p is the pressure of the hydrogen. The criterion for ambipolar diffusion to be dominant (to an error of less than one percent) is $p_i/p \ll 10^{-6}/p^2$. This indicates that extreme purity is required in order to measure ambipolar diffusion late in the afterglow. At a pressure of 10 mm Hg, an impurity of less than one part in 10^8 of hydrogen is necessary if the attachment process is to be neglected.

If the surfaces of the container have been cleaned during the discharge period, so that virtually no impurities are left on them, these surfaces will easily reabsorb impurities when the discharge is over. It is therefore possible that impurities present in the afterglow are lost to the walls by diffusion. The influence of the impurities can be seen by writing

$$\begin{aligned} \partial n/\partial t &= -[D_a/\Lambda^2 + hkN]n, \\ \partial N/\partial t &= -[D_i/\Lambda^2 + hkn]N, \end{aligned} \tag{9}$$

where D_i is the diffusion coefficient of the impurities. When we put numbers into these equations we find that the diffusion loss of the impurities is much larger than the rate at which the impurities are transformed into negative ions. Thus the term containing the electron density in the second equation of (9) may be neglected, and the rate of loss of the electron is determined by

$$\frac{\partial \ln n}{\partial (t/p\Lambda^2)} = -\left[D_a p + p\Lambda^2 N_0 hk \exp\left(-\frac{D_i p t}{p\Lambda^2}\right)\right]. \tag{10}$$

This equation shows that the attachment loss may be dominant in the early afterglow and negligible in the late postdischarge period. If the impurities originate on the walls of the container they must also leave the walls during the discharge pulse in a diffusion process. The product $p\Lambda^2 N_0$ is then essentially independent of p and Λ, provided that all other experimental parameters are kept constant. The process proposed here will then behave as a diffusion process as far as dependence on t, p, and Λ goes, although the attachment may be the dominant loss process of the electrons in the early afterglow. If a monomolecular layer of impurities is released from the walls during the discharge period in a container of the size used in this experiment (a cube with the side 5.5 cm), the partial pressure of the impurities would be of the order of 10^{-1} to 10^{-3} mm Hg. This quantity of impurities is sufficient to give dominant attachment loss process when the hydrogen pressure is larger than 10^{-1} mm Hg. It is thus not sufficient to have pure gas; the container must be cleaned with extreme care.

THE APPARATUS

A resonant cavity was built in the form of a parallelepiped. The three slightly different lengths of sides allowed three different resonant wavelengths for the three fundamental modes of the cavity. These wavelengths were 9.5 cm, 10.0 cm, and 10.5 cm. One mode was used by a power signal creating the plasma while the others could be used for microwave probing signals. A weak frequency-modulated probing signal was transmitted through the resonant cavity in parallel with a cavity wavemeter. After passing through the two cavities, the probing signal was rectified and observed as a function of time on an oscilloscope screen. The input and output couplings to the probing modes were so small that they had no measurable effect on the resonant frequency of that mode.

A photomultiplier and a slit system was moved along one of the walls of the cavity. The signal from the photomultiplier, displayed on an oscilloscope screen, reproduced the distribution of light from the plasma perpendicular to the wall at any chosen time. The light distribution at the end of the discharge pulse was used as a qualitative measure of the initial spatial electron distribution of the decay period.

The discharge plasma was contained in a cubical quartz bottle placed in the center of the microwave cavity. The bottle was connected to a vacuum system and a hydrogen supply. The influence of the fundamental diffusion length was found by using two quartz bottles of different sizes. The discharge pulses were repeated at a rate of 10–60 per second, and the pulse length could be varied from 50 msec to 0.5 μsec.

The vacuum system could reach a holding vacuum of 10^{-10} mm Hg after 24 hours. The hydrogen supply consisted of a quartz tube containing uranium hydride and a high-vacuum metal valve. The uranium hydride was made in the following way. The quartz tube was filled with uranium metal filings and baked at 800°C until a holding vacuum of less than 10^{-9} mm Hg was reached. Hydrogen was then let into the system and uranium hydride formed at about 100°C. When the hydride was heated to about 250°C, the hydrogen was released.

Contamination of the hydrogen during the discharge was a most serious problem even with the best baking,

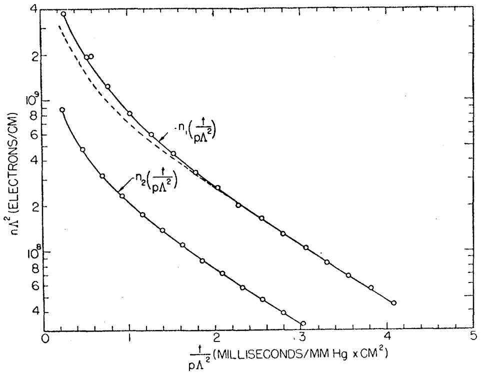

FIG. 1. The decay of electron density in hydrogen.

discharge cleaning, and vacuum techniques. The hydrogen could be shown to react with the quartz bottle during the discharge pulse. To avoid this reaction, the shortest possible discharge pulse, 0.5 μsec, was used.

MEASUREMENTS

Since it was found during the course of the investigation that impurities were produced during the discharge period, we were forced to use a short pulse length to achieve satisfactory purity. These short pulse lengths produced asymmetric spatial distributions of the discharge. In order to cover as large a pressure range as possible without changing the spatial distribution of the discharge, we found it experimentally necessary to use a very asymmetric discharge where high diffusion modes were prominent. However, if the diffusion process is the only loss mechanism, curves plotted against the proper variables for diffusion, $\langle n\rangle\Lambda^2$ and $t/p\Lambda^2$ should have the same shape, independent of the initial electron density, as long as the initial spatial distribution is held constnat. This is illustrated in Fig. 1. When these two curves are superimposed by sliding one of them in the vertical direction, they coincide within experimental error.

The initial spatial distribution of the electron density in the postdischarge period could be changed by varying the coupling of the input power. Figure 2 shows that when the initial distribution is very asymmetric the density decays very rapidly in the early afterglow, compared with the case when the initial distribution is more uniform. In the late afterglow, the two decay curves are parallel. This behavior is expected if higher diffusion modes are present. A higher density at the walls of the container would put a greater electron density in the higher diffusion modes than would be the case for a uniform distribution. Since the higher modes decay faster than the fundamental, this would explain the behavior of the curves. When the electron density has decayed to a point where only the fundamental diffusion mode is present, the density decay should be independent of the initial conditions, as illustrated.

Typical of the range of data covered by this experiment are the curves of Fig. 3. The initial spatial distribution is the same for all curves, although the initial densities vary from pressure to pressure. Since the data are plotted in terms of the proper variables for diffusion, $\langle n\rangle\Lambda^2$ and $t/p\Lambda^2$, if the data fit the ambipolar diffusion theory they should coincide when displaced vertically. The result of such normalization is shown in Fig. 4. Data were taken for other initial spatial distributions; for each constant distribution they exhibited a similar good fit with the diffusion variables.

CONCLUSION

The measurements shown above demonstrate that the diffusion mechanism is the dominant loss process of the electrons in the afterglow of pure hydrogen. Our discussion of the attachment loss process and impurities originating on the walls of the quartz bottle, as well as the necessity of using short discharge pulses to obtain purity, indicate that an attachment process may have been present in the early afterglow. The presence of higher diffusion modes made it impossible to establish this process in a more positive manner. Measurements of small amounts of impurities were quite outside the scope of this investigation. Fortunately, the result of the measurements in the late afterglow enabled us

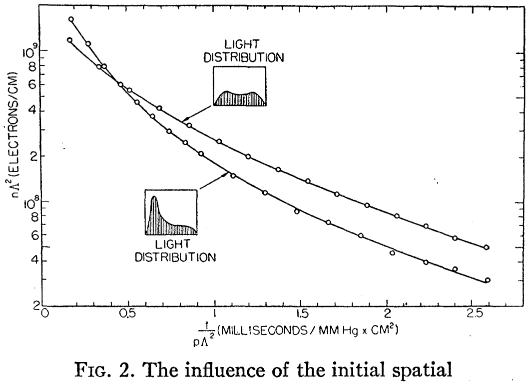

FIG. 2. The influence of the initial spatial distribution on the decay of electron density.

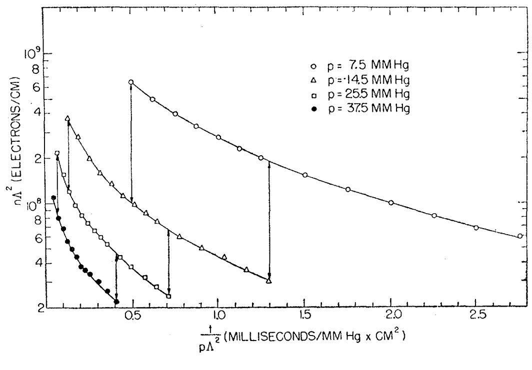

FIG. 3. Experimental runs of electron density decay at different pressures with constant initial electron distribution.

to draw definite conclusions. It can be seen from Fig. 4 that it takes considerable time for the higher diffusion modes, and possibly the attachment process, to disappear and leave the fundamental diffusion mode alone. In some cases, this does not occur until the average electron density is too small to be measured. It is therefore convenient to define an effective $D_a p$ as

$$(D_a p)_e = \frac{\partial \ln(\langle n \rangle \Lambda^2)}{\partial (t/p\Lambda^2)}.$$

This can be determined from the slope of the decay curves. It is plotted in Fig. 5. It is obvious from this figure that the effective diffusion coefficient multiplied by the pressure is not constant in the presence of the higher diffusion modes and possibly the attachment process. The value of $(D_a p)_e$ when only the fundamental diffusion mode is present can be taken as the true $D_a p$. For pure hydrogen this experiment gives $D_a p = 700 \pm 50$ cm^2-mm Hg sec^{-1}.

Although it has been stated that decay curves taken at different initial electron densities and with the same spatial distribution have the same slope within experimental error, they do not coincide exactly. The dotted line on Fig. 1 illustrates the degree of departure allowable experimentally when the lower curve is displaced to coincide with the upper one. This deviation from similarity in shape could be attributed to other loss mechanisms than diffusion. If significance is attributed to this deviation (which is within experimental error) and it is attributed to recombination, we conclude that this recombination is less than 3×10^{-8} cm^{-3} sec^{-1}.

COMPARISON WITH PREVIOUS RESULTS

In 1949, Biondi and Brown[1] surveyed the electron-ion recombination losses in a number of gases and reported their findings in hydrogen to yield a recombination coefficient of 2.5×10^{-6} cm^3/sec, independent of the pressure between 3 and 12 mm Hg. They used "spectroscopically pure" gas and relatively long discharge pulses of 250 μsec. Richardson and Holt[2] subsequently studied the same problem and found a recombination coefficient of 6.2×10^{-6} cm^3/sec, independent of the pressure between 7 and 20 mm Hg, but in the lower pressure region rising from 2×10^6 at 1 mm Hg to 6.2×10^6 at 7 mm Hg. They also used "spectroscopically pure" gas but a smaller discharge pulse of 10 μsec. Varnerin[3] reported his results for hydrogen recombination to be somewhat similar. He found a constant recombination coefficient at pressures between 30 and 50 mm Hg, but a changing recombination coefficient below this pressure rising from 3×10^{-7} at 3 mm Hg to 2.5×10^{-6} at 30 mm Hg. Varnerin paid much more attention to purity, diffusing his hydrogen through hot palladium and baking his discharge tube thoroughly to outgas it. He used a discharge pulse of 1 μsec.

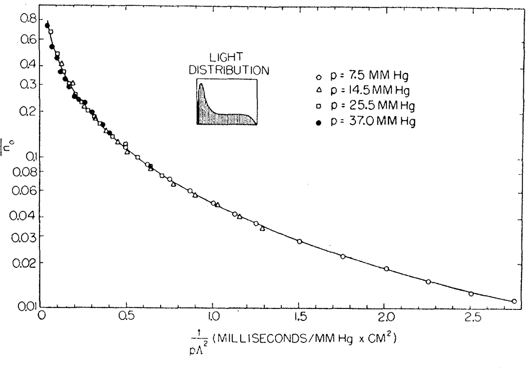

FIG. 4. The data of Fig. 3 normalized to the same initial electron densities.

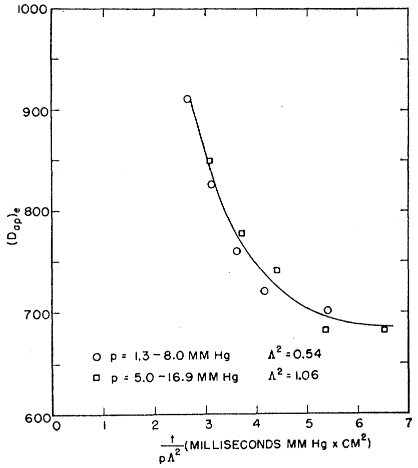

FIG. 5. Variation of the diffusion coefficient with time in the afterglow.

All of these determinations fall into the following pattern: The more carefully the purity of the gas is controlled, the lower the coefficient. At higher pressures (where collisions with impurities are more likely) the coefficient is higher. At low pressures, the shorter the discharge pulse (less contamination from the walls), the lower the coefficient. The criterion for electron-ion recombination used by all of these workers was the linear relation between the time and the reciprocal of the electron density. Characteristic of all of these cases also was the fact that the time range within which the recombination process was measured was less than the fundamental diffusion decay time. All of these facts, coupled with the results of the present investigation, support the conclusion that the previously measured recombination coefficients in hydrogen were not values characteristic of the pure gas.