Measurement of Electron-Ion Recombination*

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Microwave techniques are applied to the measurement of the recombination between electrons and positive ions. The measured recombination coefficients for monatomic gases range from 1.7×10^{-8} cc/ion-sec. for helium to 3×10^{-7} cc/ion-sec. for argon. The recombination coefficients for diatomic gases range from 2.5×10^{-6} cc/ion-sec. for hydrogen to 2.8×10^{-7} cc/ion-sec. for oxygen. At electron temperatures of 300°K, the recombination is found to be independent of pressure for the monatomic gases. A pressure dependence is observed in diatomic gases, the recombination increasing with increasing pressure in nitrogen and oxygen.

RECOMBINATION between electrons and positive ions has been studied semiquantitatively over a period of years. In the present experiment, microwave techniques are used to obtain quantitative measurements of recombination coefficients for a number of monatomic and diatomic gases.

I. EXPERIMENTAL METHOD

The recombination is measured by observing the decay of electron density from an initially ionized gas. The details of the method have been described in an earlier paper.[1] The electron density is determined from the change in resonant frequency of a microwave cavity enclosing the electrons. Under proper experimental conditions, the change of resonant frequency, $\Delta\nu$, is linearly proportional to the electron density within the cavity

$$\Delta\nu=\nu-\nu_0=Cn_-,$$

where ν is the resonant frequency of the cavity containing electrons; ν_0 is the resonant frequency of the cavity in the absence of electrons; C is a geometrical coefficient which takes into account the distribution of electrons and electric field within the cavity, and n_- is the average electron density within the cavity.

The gas sample is contained in a quartz bottle placed within a TM_{010}-mode cavity which is resonant at approximately 3000 Mc/sec. An electrodeless discharge is produced within the bottle by the application of a large microwave field to the cavity by means of a magnetron. The discharge is terminated by turning off the magnetron, and the electrons and ions remaining come to equilibrium with the gas in less than 50 μsec. Their energies from this time on are therefore thermal. If the gas pressure is sufficiently high, the diffusion loss of electrons and ions to the walls of the bottle will be small compared to the loss by volume recombination. As a result, the electron density decays with time in a manner characteristic of recombination loss. We determine the decay of electron density during the interval by measuring the resonant frequency of the cavity as a function of time.

II. MEASUREMENTS

The rate of removal of electrons or ions by recombination is given by

$$\partial n_-/\partial t=\partial n_+/\partial t=-\alpha n_+n_-$$

where n refers to charge density and α is the recombination coefficient. Under experimental conditions, $n_+\simeq n_-$, so that we have

$$\partial n/\partial t=-\alpha n^2,$$

whose solution is

$$1/n=1/n_0+\alpha t,$$

where n_0 is the electron density at time $t=0$.

Experimentally, it was found that plots of $1/n$ *vs.* t were linear, and it was concluded that recombination was taking place. However, the recombination coefficients obtained from the data were several orders of magnitude greater than those previously reported in the literature. To test the hypothesis that recombination was taking place, a search was made for light emitted from the ionized gas after the ionizing field was removed. An afterglow was found which lasted for more than 4000 μsec. after the discharge was terminated. This prolonged afterglow is most simply explained on the basis of radiative recombination.

III. RECOMBINATION IN MONATOMIC GASES

The results of measurements of electron removal in helium have been presented previously.[1] The value of the recombination coefficient at an electron temperature $T=300$°K was found to be 1.7×10^{-8} cc/ion-sec. The value was obtained with several different samples of helium and is believed to be accurate to 5 percent.

Neon has been studied most extensively for two reasons; the commercially prepared gas samples are sufficiently pure to give reproducible results for many different samples of neon, and recombination is the dominant electron removal process over a wide range of experimental variables. An example of the accuracy possible in the determination of α is illustrated by the data shown in Fig. 1. The slope of the curve can be

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[1] M. A. Biondi and S. C. Brown, Phys. Rev. **75**, 1700 (1949).

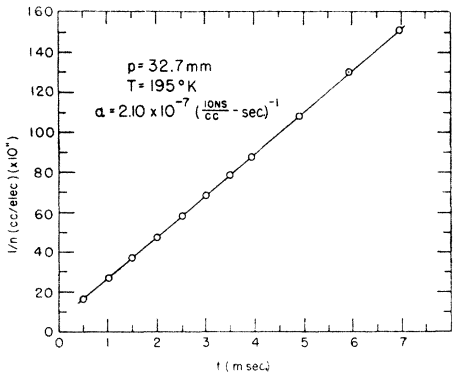

FIG. 1. Electron-ion recombination in neon at $T=195°$K.

determined very accurately so that the measurements of the recombination as a function of energy, which will be discussed shortly, are quite accurate.

The variation of the recombination coefficient with pressure was studied first. At $T=300°$K, there was no observed variation over the range $p=15$ mm Hg to 30 mm Hg. The value of α is $2.07\pm0.05\times10^{-7}$ cc/ion-sec. Next, the variation of α was studied over a temperature range from $T=300°$K to 410°K. No change in α with temperature was found. (The maximum change observed was 5 percent but did not follow a consistent trend.)

No variation having been found in the recombination coefficient at elevated temperatures, the behavior of α as a function of pressure was studied at the temperature of dry ice (195°K) and liquid nitrogen (77°K). At 195°K, no variation in α with pressure was found, and the value of α was found to be the same at 195°K as at 300°K. At 77°K, a change in the behavior was noted. The value of the recombination coefficient increased with increasing pressure; however, at low pressures, the value of α approached the same value as at 195° and 300°K. These results are shown in Figs. 2 and 3. Figure 2 indicates that the recombination is independent of pressure at 195°K and 300°K over the measured range. At 77°K, a strong pressure dependence develops; however, the residual value of α (the value of α in the limit $p\rightarrow0$) is the same as for $T=195°$ and 300°K. Empirically, it is found that the recombination coefficient at 77°K is given by

$$\alpha=\alpha_r+Ae^{bp},$$

where

$$\alpha_r=1.94\times10^{-7}\text{ cc/ion-sec.}$$
$$A=0.13\times10^{-7}\text{ cc/ion-sec.}$$
$$b=0.16\text{ (mm Hg)}^{-1}.$$

α_r is called the residual part of the recombination coefficient since it does not seem to depend on energy or pressure. The pressure dependent part, $\alpha(p)=Ae^{bp}$, is shown in Fig. 4. No physical explanation for the exponential character of the pressure dependent part of α is available at present; however, attempts to fit the data to a $p^n(n=1, 2, 3, 4)$ type of dependence do not give a reasonable result.

The measurements of argon are of a less satisfactory nature because we have been unable to obtain sufficiently pure gas samples to give adequately reproducible results. However, by averaging the data obtained from a number of samples of argon, we find that the residual part of the recombination coefficient is approximately

$$\alpha_r=3\times10^{-7}\text{ cc/ion-sec.}$$

at $T=300°$K.

The values of the coefficient of recombination between thermal electrons and ions are several orders of magnitude greater than those previously reported in the literature.[2,3] The value of α increases with increasing mass number. Except at low temperatures, α appears to be independent of pressure over the measured range, and in neon is also independent of temperature.

IV. RECOMBINATION IN DIATOMIC GASES

Over the measured range, the recombination coefficient for hydrogen is found to be independent of pressure at $T=300°$K. The results are shown in Fig. 5. Studies of the energy dependence of α for hydrogen in the temperature range from 303°K to 413°K indicate that α varies as $1/T^k$ where the value of k is between 0.8 and 0.9.

The recombination coefficient for nitrogen is about half the value for hydrogen and a rise in the recombination coefficient is noted with increasing pressure (see Fig. 5). A more marked pressure dependence is observed in oxygen and the residual value of α is about one-fifth the value for nitrogen.

The behavior of the recombination coefficients for diatomic gases is quite different from that for monatomic gases. We find a dependence of α on temperature for hydrogen, while for neon we found that the residual value of α is independent of temperature. In addition,

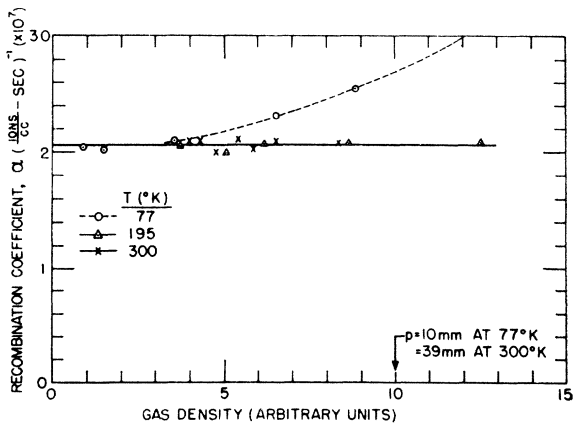

FIG. 2. Recombination in neon as a function of gas density and temperature.

[2] F. L. Mohler, Phys. Rev. **31**, 187 (1928).
[3] C. Kenty, Phys. Rev. **32**, 624 (1928).

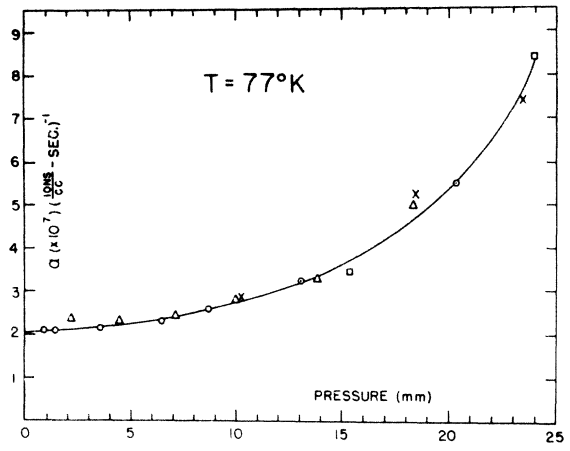

FIG. 3. Recombination in neon at the temperature of liquid nitrogen.

the recombination coefficients are observed to increase with increasing atomic number for monatomic gases while they decrease with increasing atomic number for diatomic gases.

The lack of pressure dependence for the recombination at low pressures indicates that this recombination is a two-body process involving the direct capture of the electron by the ion. In monatomic gases, the capture is believed to be by radiative transitions of the electron into excited levels of the resulting atom. However, the fact that the recombination coefficient for hydrogen is more than 100 times that of helium indicates that there exists for diatomic ions a capture mechanism which is much more efficient than radiative capture. The spacing of the vibration and rotation levels of diatomic ions is the same order of magnitude as the average electron energy. It is suggested that these levels offer an efficient means of absorbing the electron's initial kinetic energy into vibration and rotation energy of the resulting excited molecule. The subsequent radiation of quanta removes enough energy from the excited molecule to prevent dissociation into an electron and an ion.

V. THEORY

The existing theories of recombination[4–6] predict electron-ion recombination coefficients which are 10^4 times smaller than the values reported here. The theories formulate quantum mechanically the transition probability of electrons with positive initial energy into excited levels of the resulting atom. From these theories, it is concluded that the significant contributions to the recombination come from transitions to ground state and the low lying excited levels. Craggs and Hopwood[6] compare their measurement of the recombination of electrons with H^+ with theory and conclude that transitions to ground state are sufficient to account for their observed value. In the present experiment, we do not arrive at this conclusion. We shall calculate the recombination arising from the transitions of electrons into the highest excited states by computing the continuous radiation emitted by an electron accelerated in the field of the ion.

The calculations of Kramers and Eddington[7] on opacity and absorption cross sections may be adapted to this method. If we require that an electron of initial velocity, v, radiate its initial kinetic energy or more in order to be captured, we can calculate a critical capture orbit, and, from this, the capture cross section. The capture cross section for thermal electrons is given by

$$\sigma = 8.64\left\{\frac{Z_e^{8/5}e^4}{m^2c^{6/5}v_i^{14/5}}\right\}\text{cm}^2$$

where σ is the capture cross section; Z_e is the effective charge of the ion; e and m are the electron charge and mass, respectively, and c is the velocity of light.

The coefficient of recombination for monoenergetic electrons of velocity, v, is given by $\alpha(v)=\sigma v$. The observable recombination coefficient $\alpha(T)$ is obtained by averaging the recombination over the Maxwellian energy distribution of the electrons; thus

$$\alpha(T) = 14.5(m/2kT)^{0.9}\left\{\frac{Z_e^{8/5}e^4}{m^2c^{6/5}}\right\}\text{cc/ion-sec.}, \qquad (1)$$

where T is the electron temperature.

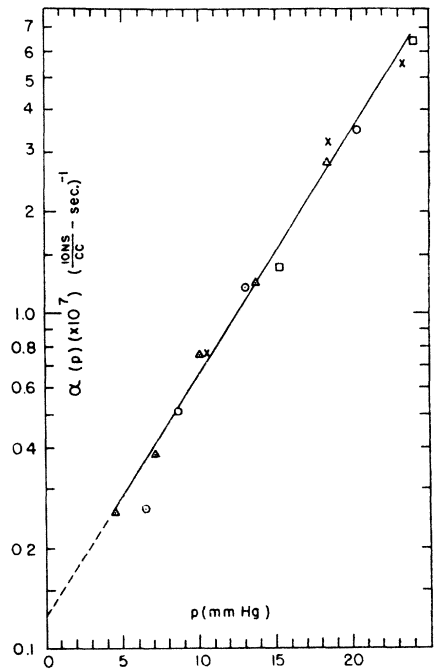

FIG. 4. The pressure-dependent part of the recombination coefficient for neon at $T=77°K$.

[4] See, for example, P. M. Morse and E. C. G. Stueckelberg, Phys. Rev. **35**, 116 (1930).
[5] H. Zanstra, Proc. Roy. Soc. **A186**, 236 (1946).
[6] J. D. Craggs and W. Hopwood, Proc. Phys. Soc. **59**, 771 (1947).
[7] A. S. Eddington, *The Internal Constitution of the Stars* (Cambridge University Press, London, 1926), p. 224.

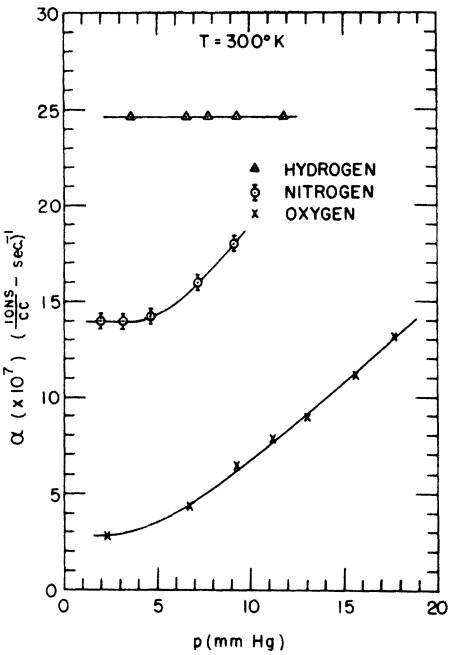

FIG. 5. Recombination in diatomic gases at $T=300°K$.

It is found that according to the classical calculation, the electron's orbit penetrates the electronic shell of the ion and hence the electron is accelerated in a field arising from a variable charge. Using the quantum-mechanical model of the helium ion and the Thomas-Fermi model for the neon and argon ions, we may calculate the effective ion charge, Z_e, at the distance of closest approach of the electron to the ion. For thermal electrons, the value of Z_e for helium is approximately 2, for neon, it lies between 8 and 9 and for argon, between 11 and 13. Since most of the energy is radiated while the electron is close to the ion, the use of these values of Z_e in Eq. (1) introduces only a small error in the calculation. The values of $\alpha(T)$ obtained from this theory for $T=300°K$ are compared with experimental values in Table I. The theory predicts an order of magnitude more recombination than is observed; however, it predicts the relative values of α in going from He to A quite accurately. The capture condition, that an electron which radiates its initial kinetic energy is trapped, is a minimum condition. If one were to impose more stringent capture conditions, the discrepancy between theory and experiment would be reduced.

VI. DISCUSSION

The theories of recombination all predict an energy dependence for α. The measurements in neon show no energy dependence while measurements in hydrogen indicate an energy dependence in agreement with the present theory. The better agreement between the present theory and experiment compared to the previous quantum-mechanical theories suggests that transitions to high lying excited levels play an important role in recombination between thermal electrons and ions. A quantum-mechanical theory which accurately takes into account this process is necessary.

The measured recombination coefficients for monatomic and diatomic gases lie in the range 10^{-8} to 10^{-6} cc/ion-sec. These values are several orders of magnitude greater than previous experimental values and are of the order of previously reported values of positive ion–negative ion recombination coefficients. However, the present experiment measures the removal of electrons since the apparatus is sensitive to electrons and ions in the inverse ratio of their masses.

TABLE I. Recombination coefficients at $T=300°K$.

Gas	$\alpha[T]$(theory)	α(measured)	Ratio of values
He	2.0×10^{-7}	1.7×10^{-8}	12
Ne	2.2×10^{-6}	2.03×10^{-7}	11
A	3.3×10^{-6}	3×10^{-7}	11

The gas samples used were obtained from the Air Reduction Sales Company. The vacuum system was of glass and quartz and used a mercury McLeod gauge and a mercury cut-off. The system was thoroughly outgassed before each run and held for several hours at 10^{-7} mm Hg when isolated from the pumps. The helium and neon samples were purified by a liquid nitrogen-cooled charcoal trap while the other gases were passed through two liquid nitrogen traps.