

Electron Recombination and Collision Cross-Section Measurements in Hydrogen*

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Electron densities and mean collision cross sections are deduced from measurements of the propagation constant for microwaves in a plasma. From the electron collision cross-section measurements, inferences are drawn concerning the slope of the cross-section electron velocity curve. The measurements are compared with those made by electron beam techniques. From the electron density measurements the recombination coefficient of hydrogen as a function of pressure is obtained. These data are interpreted on the basis of dissociative and ion-ion recombination.

I. INTRODUCTION

THE measurement of the decay of electron density in a plasma has been made possible by the use of microwave techniques. Biondi and Brown^{1,2} were able to identify both recombination and diffusion modes of decay. Their method was based on a measurement of the shift in resonant frequency of a microwave cavity containing a decaying plasma. This method, which initially determined only the inductive loading of the cavity by electrons and not the resistive component, has been extended by Phelps, Fundingsland, and Brown³ in the preceding paper to measure the resistive component. The resistive component is of primary importance in determining the collision cross section of electrons with gas molecules. These methods employed resonant devices. The method to be discussed here involves no resonant structures and depends on the propagation constant of microwaves in a section of rectangular wave guide containing the plasma.

II. METHOD

A plasma is established by a one-microsecond rf magnetron pulse in a section of 10-cm band wave guide as shown in Fig. 1. The discharge tube is electrically one-half wavelength long with a quarter wavelength block of quartz against the shorted end of the wave guide. The gas is confined in a quarter wavelength section of guide. The quartz block is used to prevent ionization in that section of the tube. In a tube without a quartz block, relatively little ionization occurs in the $\lambda_g/4$ section nearest the shorted end of the wave guide because the voltage standing wave is low there. The vacuum seal is made with a glass window sealed to a Kovar frame. The metal parts of the tube are made of silver-plated Kovar joined by means of high temperature brazing alloys.

During the decay period, the plasma will rapidly tend to uniformity if the dominant electron loss mechanism is that of recombination. This results from the fact that the rate of electron loss is proportional to

the square of the density, so that local high concentrations are more rapidly recombined.

A glass three-stage oil diffusion pump was used with the vacuum system. Only metal stopcocks were used. A mercury manometer and McLeod gauge were used to measure pressure. The tube was isolated from the mercury by a single liquid air trap during bakeout and by a second trap during measurement. Hydrogen obtained through a palladium leak was used for study.

Measurements are made during the plasma decay period after the electrons have come to thermal equilibrium with the gas. By means of a weak rf probing signal, measurements of voltage standing wave ratio and phase are made in the line as a function of time. The method of transient standing wave measurements is essentially the same as that of reference 3. With these measurements, the transmission line equations can be used to determine the characteristic impedance of the gas tube at the gas-glass window boundary looking into the tube.

The impedance of the measuring tube normalized with respect to the empty guide impedance at the gas-glass window boundary is given by

$$z = j(2\pi/k\lambda_g) \operatorname{ctnh}(k\lambda_g/4), \quad (1)$$

where k is the propagation coefficient of the gas section and λ_g is the guided wavelength of the empty guide. k is given by

$$k = (2\pi/\lambda_g) [-1 + j(\sigma_c/\omega\epsilon_0)(\lambda_g/\lambda_0)^2]^{1/2}, \quad (2)$$

where σ_c is the complex conductivity of the plasma, ω the radian frequency of the electric field, and ϵ_0 the permittivity of free space.

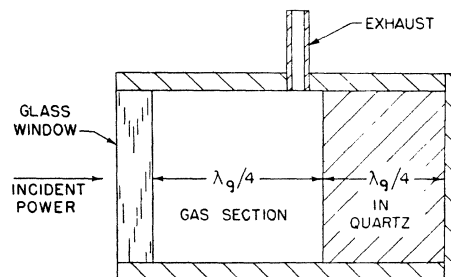


FIG. 1. Measuring tube.

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

² M. A. Biondi and S. C. Brown, *Phys. Rev.* **76**, 1697 (1949).

³ Phelps, Fundingsland, and Brown, *Phys. Rev.* **84**, 559 (1951).

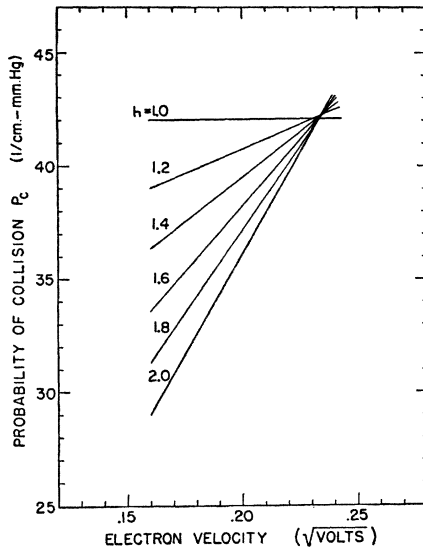


FIG. 2. Probability of collision as a function of electron velocity.

The complex conductivity, σ_c , can be determined experimentally as a function of time from the type of experiment described above and the use of Eqs. (1) and (2). Basically the absolute magnitude of σ_c and the ratio of real to imaginary parts σ_r/σ_i are determined.

III. ANALYSIS OF COLLISION CROSS-SECTION DATA

Measurements of σ_r/σ_i as a function of pressure were made for different pressures in the range 1.5 to 50 mm Hg. From the theory of reference 3, P_c can be represented by

$$P_c = av^{h-1}. \quad (3)$$

If a value of h is assumed, a value of a can be calculated for which the theory best represents the data. In Fig. 2, a tentative set of curves for $P_c(v)$ is obtained. It is noted that all curves agree in the neighborhood of $0.233 \text{ (volt)}^{1/2}$, and it is therefore believed that the experiments give

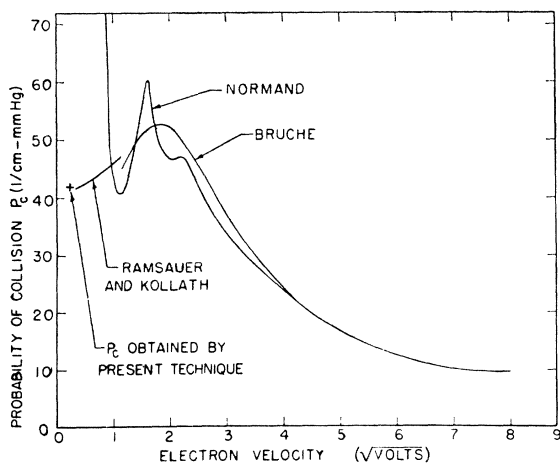


FIG. 3. Comparison of probability of collision as a function of electron velocity with data of other workers.

the value of $P_c=42$ at $0.233 \text{ (volt)}^{1/2}$ with an accuracy of about 5 percent.

Phelps, Fundingsland, and Brown calculate the quantity

$$(a\phi_0/\omega)(\sigma_i/\sigma_r)(2kT/m)^{h/2},$$

as a function of σ_r/σ_i , on the assumption embodied in Eq. (3). Multiplying the foregoing by experimental values of $\sigma_r/\phi_0\sigma_i$, one should obtain a quantity,

$$(a/\omega)(2kT/m)^{h/2},$$

which is independent of σ_r/σ_i if the correct function for $P_c(v)$ has been assumed. Choosing the value of h which renders the product most nearly constant will give the best representation of P_c as a power of electron velocity. This yields a value of $h=1.6$.

The scatter in experimental data introduces an uncertainty of about 0.2 in h , while a pressure dependent systematic error might contribute again as much uncertainty. It is reasonably well established that $h>1.0$. This means that the P_c versus electron velocity curve has a positive slope.

Experimental values of P_c are plotted as a function of electron velocity in Fig. 3. The data of Normand,⁴ Brüche,⁵ and Ramsauer and Kollath⁶ are shown. At velocities less than 1 $\text{(volt)}^{1/2}$, Normand's results differ markedly from those of the other investigators. Brüche and Ramsauer and Kollath are in substantial agreement.

Part of the information obtained by the present technique is given as a point established at $0.233 \text{ (volt)}^{1/2}$. While the slope of the curve passing through this point is not definitely established, a positive slope is fairly certain. Thus, the present measurement lends support to Ramsauer and Kollath. The nearly perfect agreement in magnitude is somewhat illusory in view of the slightly different nature of the cross section measured.³

IV. RECOMBINATION MEASUREMENTS IN HYDROGEN

The present technique has been used to study recombination phenomena in hydrogen. After the electrons have had sufficient time to come to thermal equilibrium with the gas, Biondi and Brown² found that the only mode of electron density decay that could explain the experimental results was that of recombination. This is recognized by the fact that a reciprocal density plot as a function of time is a straight line.

Data obtained by the present technique for hydrogen at room temperature are given in Fig. 4. The range of electron densities varied from 1×10^9 to 2×10^{10} electrons/cm³. The theory of reference 3 for $h=1.0$ was used in calculating densities. The density so determined is relatively insensitive to the choice of h . Previous data by Biondi and Brown² are shown in the low pressure range. The low pressure part of the curve is extremely

⁴ C. E. Normand, Phys. Rev. 35, 1217 (1930).

⁵ E. Brüche, Ann. Physik 82, 912 (1927).

⁶ C. Ramsauer and R. Kollath, Ann. Physik 4, 91 (1929).

sensitive to minute traces of impurities. Repeated bakeouts succeeded in lowering the curve somewhat with each bakeout. The tube and vacuum system were baked for one week at 330°C before taking data. After this a bakeout for four days at 340°C effected no change in the general form of the curve. Biondi and Brown used spectroscopically pure hydrogen while palladium purified hydrogen has been used in the present investigation. It is possible that the different results can be explained on this basis. Richardson and Holt⁷ reported a value of α of 2×10^{-6} cm³/electron-sec from 1 to 3 mm Hg, rising to 6.2×10^{-6} cm³/electron-sec at 7 mm Hg, remaining essentially constant to a pressure of 19.8 mm Hg. While the general type of curve they obtained resembles that of the present investigation, the absolute values are considerably different.

The shape of the curve of Fig. 4 suggests that the recombination coefficient has a pressure independent component α_0 and a pressure dependent component $\alpha(p_0)$. The measured coefficient α_m is then

$$\alpha_m = \alpha_0 + \alpha(p_0). \quad (4)$$

If α_0 is taken as 0.34×10^{-6} cm³/electron-sec, $\alpha(p_0)$ can be plotted as in Fig. 5 on a log plot. Within experimental error $\alpha(p_0)$ is proportional to p_0^2 for pressures up to 25 mm Hg. The range of data at higher pressures is insufficient to establish any clear-cut dependence on a power of pressure. $\alpha(p_0)$ is given approximately by

$$\alpha(p_0) = 0.0026 p_0^2 \text{ for } p_0 < 25 \text{ mm.}$$

Bates and Massey⁸ proposed a mechanism by which a measured recombination coefficient could represent the combined effects of a direct electron-positive ion recombination α_e plus a negative ion-positive ion recombination α_i controlled by a quasi-equilibrium between the electron and negative ion densities. In such a case the measured recombination coefficient is given by

$$\alpha_m = \alpha_e + \lambda \alpha_i, \quad (5)$$

where λ is a constant given by

$$\lambda = n_- / n_e, \quad (6)$$

and by the mass action law is proportional to p_0 if the density of neutral atom or molecule to which the electron attaches is proportional to p_0 . This mechanism might very well explain the present measurements. In the low pressure range, α_i , according to the Thomson theory,⁹ is proportional to p_0 , while at higher pressures it becomes independent of p_0 . Thus, $\lambda \alpha_i$ is proportional to p_0^2 at low pressures and to p_0 at high pressures. The p_0^2 dependence at low pressures is verified, while the

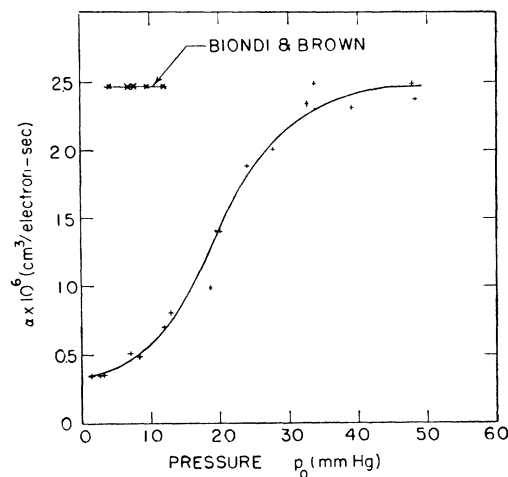


FIG. 4. Recombination coefficient in hydrogen as a function of pressure.

data at higher pressures are inconclusive in establishing the expected p_0 dependence.

The possibility that either H_1^- or H_2^- may have been present has been considered. For the case of either ion and its recombination to H_1^+ or H_2^+ , α_i can be calculated from the Thomson⁹ theory of recombination. In the case of H_2^- , λ can be inferred from the measured $\alpha(p_0)$ and the calculated α_i . From the statistical mechanical equation¹⁰ relating n_- and n_0 , one can determine the electron affinity. The electron affinity so obtained is 0.14 ev. Eyring, Hirshfelder, and Taylor¹¹ calculated the electron affinity as -2.4 ev. For this

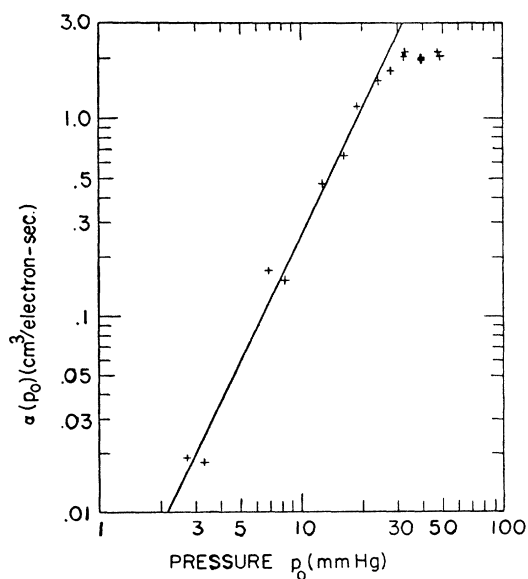


FIG. 5. Pressure dependent component of hydrogen recombination coefficient.

⁷ J. M. Richardson and R. B. Holt, Phys. Rev. **81**, 153 (1951).

⁸ D. R. Bates and H. S. W. Massey, Proc. Roy. Soc. (London) **A187**, 261 (1946).

⁹ J. J. Thomson, Phil. Mag. **47**, 337 (1924).

¹⁰ R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, London, 1929), first edition, p. 281.

¹¹ Eyring, Hirshfelder, and Taylor, J. Chem. Phys. **4**, 479 (1936).

reason, it appears that H_2^- is not involved. The existence of H_1^- remains a possibility. Calculations, such as were made for H_2^- to compare electron affinities, are not possible since the concentration of H_1 is unknown.

The pressure independent component is much too large to explain¹² in terms of a radiative recombination

¹² D. R. Bates, Phys. Rev. 77, 718 (1950).

process. Dissociative recombination, as suggested by Bates,¹³ can very well account for the observed data.

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¹³ D. R. Bates, Phys. Rev. 78, 492 (1950).

Diffusion as Hydrodynamic Motion

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A phenomenological definition of diffusion in a binary mixture suggests a description of the motion by a hydrodynamic equation which contains a frictional force proportional to the relative diffusion velocity. Plausible assumptions give a set of hydrodynamic equations for any gaseous mixture, which may include charged molecules in a magnetic field. The equations determine the diffusion velocities in terms of the applied forces, the pressure gradients, and the binary diffusion coefficients. The same equations are also derived from kinetic theory in the first diffusion approximation. In higher approximations where thermal diffusion first appears, the equations are no longer valid.

IN a previous paper¹ the motion of electrons and ions through a neutral gas in a magnetic field was analyzed with hydrodynamic equations in which frictional forces represented the retarding action of the gas. A phenomenological definition of diffusion suggested the frictional force, and its dependence on both diffusion velocity and diffusion coefficient.² Thus diffusion velocities could be related to the forces acting on each type of ion without the difficult ideas of mean free path and collision frequency. The present paper has three purposes: to state assumptions necessary for applications of the phenomenological definition; to extend previous equations, limited to ion densities small compared to the gas density, to any gaseous mixture;³ and to test the conclusions by the second approximation of kinetic theory,⁴ a procedure which shows that there is no simple way to include thermal diffusion.

¹ M. H. Johnson and E. O. Hulburt, Phys. Rev. 79, 802 (1950).

² A. Einstein introduced such a force in his well-known theory of Brownian motion. Thereafter it has been repeatedly used in the theory of electrolytes. A. Schlüter, Z. Naturforsch. 5a, 72 (1950); 6a, 73 (1951), has based a treatment of gaseous diffusion on the concept of frictional forces. He introduced the forces and evaluated the frictional coefficients in a different way than that followed in reference 1 and in the present paper. The hydrodynamic equations he obtained, explicitly given in his second paper for a mixture of two ionized and one neutral component in the presence of external fields, are essentially the same as Eq. (6) above.

³ For a preliminary report, see M. H. Johnson, Phys. Rev. 82, 298 (1951).

⁴ S. Chapman and G. T. Cowling *The Mathematical Theory of Non-uniform Gases*, Cambridge University Press, Cambridge, England (1939), Chaps. 7, 8, 9, and 18. We shall use the notation and units of this book. For symbols we have sometimes incompletely defined, the list of symbols at the beginning of the book should be consulted, where page references to all definitions will be found.

Let p_r , ρ_r , and n_r be the pressure, mass density, and number density of the r th species of molecules in a mixture of N species. Each gas is assumed to obey the ideal gas law, $p_r = n_r kT$. To define the diffusion coefficient D_{rs} , suppose the mixture consists of the two species r and s at a uniform temperature and uniform total pressure, $p = p_r + p_s$. Let the mean molecular velocities $\langle \mathbf{c}_r \rangle_{Av}$ and $\langle \mathbf{c}_s \rangle_{Av}$ at a point \mathbf{r} , t be measured in a reference frame such that $n_r \langle \mathbf{c}_r \rangle_{Av} + n_s \langle \mathbf{c}_s \rangle_{Av} = 0$. We assert as an experimental fact that the diffusion current is then given by

$$n_r \langle \mathbf{c}_r \rangle_{Av} = -D_{rs} \partial n_r / \partial \mathbf{r}. \quad (1)$$

For the coefficients so defined, $D_{rs} = D_{sr}$, which can be seen by applying the definition to the species s . To remove the restriction to a special reference frame it is only necessary to express $\langle \mathbf{c}_r \rangle_{Av}$ in terms of the velocity difference $\langle \mathbf{c}_r \rangle_{Av} - \langle \mathbf{c}_s \rangle_{Av}$; $\langle \mathbf{c}_r \rangle_{Av} = n_s (n_r + n_s)^{-1} (\langle \mathbf{c}_r \rangle_{Av} - \langle \mathbf{c}_s \rangle_{Av})$. If, at the same time, n_r is replaced by p_r through the ideal gas law, Eq. (1) may be written

$$-\partial p_r / \partial \mathbf{r} = \theta_{rs} (\langle \mathbf{c}_r \rangle_{Av} - \langle \mathbf{c}_s \rangle_{Av}), \quad (2a)$$

$$\theta_{rs} \equiv kT n_r n_s (n_r + n_s)^{-1} (D_{rs})^{-1}. \quad (2b)$$

Equation (2), which is equivalent to Eq. (1), may be applied in any reference frame for both terms are invariant to Galilean transformations.

The form of Eq. (2) suggests an equilibrium of hydrodynamic forces since the negative pressure gradient is the force exerted on a fluid in a unit volume by the fluid outside that volume. The right-hand member has the appearance of a frictional force, for it is proportional to and oppositely directed to the relative velocity of the