an amount equal to its velocity, i.e., by the condition

 $\langle (\Delta \mathbf{v})^2 \rangle = \langle (\mathbf{v})^2 \rangle,$ 

where

$$\Delta \mathbf{v} \equiv e/m \int_0^\tau \mathbf{E}(t_1) dt_1, \qquad (9a)$$

then the restriction on s is  $s \ll \tau$ . We can estimate the order of magnitude of  $\tau$  by using Eq. (8a) in Eq. (9a) even though **E**, the field produced by the perturbers in Eq. (8a), is at a fixed point in space whereas **E** in

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### **Recombination of Ions and Electrons**

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A process of electron-ion recombination is considered, involving three bodies (one ion and two electrons), in which an electron, as a result of a collision with another electron, loses enough energy to be captured in one of the excited electronic orbits of the ion and then ends in the ground state by emission of one or more light quanta. It is shown that such a process might account for the large values of the recombination coefficient found experimentally.

#### I. INTRODUCTION

 $\mathbf{R}^{\mathrm{ADIATIVE}}$  recombination is the process in which an electron comes within a small distance of a positive ion and is captured in one of the low-lying electronic orbits, with the emission of a light quantum. Quantum mechanical calculations <sup>1,2</sup> on such a process predict recombination coefficients of the order of 10<sup>-12</sup> cm<sup>3</sup>/sec. Experimentally, recombination in many gases has been studied and in all those cases in which it is almost certain to occur between positive ions and electrons, recombination coefficients of the order of 10<sup>-10</sup> cm<sup>3</sup>/sec have been found.<sup>3-5</sup> So far none of the many processes considered to eliminate such a discrepancy seems to account for the large recombination coefficients found experimentally. "Neither dissociative recombination nor effects due to negative ions are likely to be important in the gases investigated."6

The purpose of this paper is to show that there is a process of electron-ion recombination which might account for the values of the recombination coefficients found experimentally. Consider a fully ionized gas, consisting entirely of singly charged ions and electrons. A

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(1930).
<sup>2</sup> G. Cillié, Roy. Astron. Soc. M. N., **32**, 820 (1932).
<sup>8</sup> C. Kenty, Phys. Rev. **32**, 624 (1928).
<sup>4</sup> F. L. Mohler, J. Research Natl. Bur. Standards **19**, 447, 559

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<sup>5</sup> J. D. Craggs and W. Hopwood, Proc. Phys. Soc. (London)
59, 771 (1947).
<sup>6</sup> H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic*

Impact Phenomena (Clarendon Press, Oxford, 1952).

process is possible, involving three bodies (one ion and two electrons), in which an electron, as a result of a collision with another electron, loses enough energy to be captured in one of the excited electronic states of the ion and then ends in the ground state by emission of one or more light quanta. This process is by no means new and has been considered implicitly, for instance, in the study of stellar atmospheres.<sup>7</sup> It appears, however, to have been somehow overlooked in the explanation of any one of the recombination experiments mentioned above.

Eq. (9a) is the field at the moving perturber. The result

 $\tau = \left(\frac{\lambda}{v}\right) \left(\frac{\lambda}{d}\right)^3 \frac{36\pi}{\ln(\lambda/a)},$ 

where  $d = n^{-\frac{1}{3}}$  and a is a lower cutoff distance [replacing

 $\rho_c$  in Eq. (8a)] that can be taken as the mean distance

of closest approach. Since  $\tau$  is much greater than  $(\lambda/v)$ ,

it is possible to have s large enough to guarantee Eq.

The calculations presented here are for the case of a fully ionized hydrogen gas. The conclusions arrived at might be expected to be at least qualitatively valid also for other atomic gases.

#### II. THEORY

Consider a fully ionized hydrogen gas. As a result of a collision between two electrons, one of them may lose enough of its kinetic energy to be captured in a close orbit around an ion (say in a state of total quantum number n and orbital angular momentum l). Once the electron is bound, either of two processes can occur: (a) The electron is re-ejected into the continuum by collision with another electron, or (b) the electron makes a radiative transition to a lower level, from which it can still be re-ejected into the continuum or make another radiative transition. Recombination will be

(10a)

<sup>&</sup>lt;sup>7</sup> R. G. Giovanelli, Australian J. Sci. Research A1, 275, 289 (1948).

TABLE I. Transition probabilities for hydrogen in 10<sup>8</sup> sec<sup>-1</sup>.

n	$np \rightarrow 1s$	$nd \rightarrow 2p$	$nf \rightarrow 3d$	$ng \rightarrow 4f$	$nh \rightarrow 5g$	$ni \rightarrow 6h$	$nl \rightarrow 7i$	$nm \rightarrow 8$
2	6.25							
3	1.64	0.64						
4	0.68	0.204	0.137					
5	0.34	0.094	0.045	0.043				
6	0.20	0.048	0.021	0.014	0.016			
7	0.10	0.026	0.012	0.0087	0.010	0.007		
8	0.07	0.015	0.005	0.0059	0.0068	0.0047	0.0034	
9	0.05	0.010	0.0045	0.0041	0.0048	0.0033	0.0023	0.0017

considered accomplished when a neutral hydrogen atom is formed in its ground state.

The present picture neglects collisional transitions between quantized states. This may be justified by the fact that the rates of such transitions do not usually exceed the rates of collisional ionization.7 Furthermore, collisional transitions are mostly to neighboring states and they may be expected to compensate to some extent to the effect of the present calculations. Captures of electrons to the *n*th state are assumed to be distributed among the substates of different angular momenta according to their statistical weights. Elastic collisions in which an atom goes from a sublevel l to another sublevel r of the same level are considered unimportant. This seems very likely to be the case on the basis of Giovanelli's analysis.<sup>7</sup> To compute the rates of threebody recombinations which end up in hydrogen atoms in the ground state, we need to know the rates of threebody recombination to each level, the probabilities of collision ionization and of radiative transitions from each level. The rate of three-body recombination to a state j is<sup>7</sup>

$$\frac{N_+N_e^2}{\pi m^2} \left(\frac{h}{k\theta}\right)^3 \frac{\epsilon^4 \omega_j K_j}{\omega_i},$$

where  $\theta$  is the electron temperature and  $E_i^{i}$  the ionization energy of level j.  $N_+$  and  $N_e$  are ion and electron densities,  $\epsilon$  and m the charge and the mass of the electron,  $\omega_i$  and  $\omega_i$  the weights of the *j* state and of the ionized state, respectively. Also

$$K_{j} = \int_{0}^{+\infty} \frac{\alpha \exp(-\alpha/k\theta) d\alpha}{E_{j}^{i}(E_{j}^{i} + \alpha)}.$$

For  $E_i^i/k\theta > 1$  the integral is approximately equal to  $(k\theta/E_i)^2$ ; for  $E_i/k\theta < 1$  to  $k\theta/E_i$ . The above rate of three-body recombination is obtained from the principle of detailed balancing and the classical cross section for collision ionization of Thomson<sup>8</sup> and Bohr.<sup>9</sup> The collision ionization probability from state n is given by

$$\frac{N_e}{(\pi m)^{\frac{1}{2}}} \left(\frac{2}{k\theta}\right)^{\frac{3}{2}} 2\pi \epsilon^4 K_n \exp(-E_n^{i}/k\theta),$$

where  $K_n \approx (k\theta/E_n^i)^2$  for  $E_n^i/k\theta > 1$  and  $K_n \approx k\theta/E_n^i$  for  $E_n^i/k\theta < 1.$ 

The transition probabilities (for hydrogen) from a state of principal quantum number n and orbital quantum number l to a state n'l' are given in Table I. Up to n=6 they are taken from Bethe and Salpeter.<sup>10</sup> For n=7, 8, and 9 the transition probabilities for  $7i \rightarrow 6h, 8l \rightarrow 7i, 9m \rightarrow 8l$  have been extrapolated from the  $2p \rightarrow 1s$ ,  $3d \rightarrow 2p$ ,  $4f \rightarrow 3d$ ,  $5g \rightarrow 4f$ ,  $6h \rightarrow 5g$ transition probabilities. This procedure is quite safe for the kind of answer one requires from these calculations. For each state n, l only the transition to the state n'=l, l'=l-1 has been considered, i.e., the transition to the state of lowest energy which is compatible with the selection rules. To illustrate this point, in Table II the relative transition probabilities are given from the 5d state. They are taken from Bethe and Salpeter.<sup>10</sup> The lifetimes of the ns levels are very long, because transitions  $ns \rightarrow n'p$  require a change of n and l in opposite sense. Therefore the contribution of threebody captures in s states to the total rate of recombination is very small, when account is taken also of the small satistical weight of the s states.

The lifetimes of the 7, 8, and 9 states have been assumed according to the rule that, for a fixed value of the orbital angular momentum l, the lifetime  $T_{nl}$  is proportional to  $n^3$  (n = total quantum number).

The rates of three-body recombinations have been calculated for a number of densities and temperatures. The procedure consists in "following" an electron which, as a result of a collision with another electron, has been captured in one of the substates of the nth level and in determining the probability that it finally ends in the ground state. Consider, for instance, electrons captured by collision into the 3d state, at a rate R. From the 3d state the electron can either be re-ejected into the continuum or make a transition to the 2pstate. Let  $P(3d \rightarrow 2p)$  be the probability that the second event occurs. The contribution of the 3d state to the rate of three-body recombination is then given by  $RP(3d \rightarrow 2p)P(2p \rightarrow 1s)$ .

In Table III the rates of three-body recombinations from captures into states of principal quantum number *n* are given for an electron temperature  $\theta = 1000^{\circ}$ K and electron densities  $n_e = 10^{12}$ ,  $2 \times 10^{12}$ ,  $5 \times 10^{12}$ , and  $10^{13}$ cm<sup>-3</sup>. Captures to levels with  $n \gtrsim 10$  seem to contribute only little to the total rate of recombination. The maxi-

TABLE II. Relative transition probabilities from the 5d state.

$4f \rightarrow 3d \rightarrow 2p \rightarrow 1s$ $4p \rightarrow 3d \rightarrow 2p \rightarrow 1s$ $4t \rightarrow 2t \rightarrow 1s$	$0.3\% \\ 0.1\% \\ 0.2\%$	$\begin{array}{c} 4p \longrightarrow 2s \\ 3p \longrightarrow 2s \end{array}$	$\frac{1.1\%}{2.9\%}$
$4p \rightarrow 3s \rightarrow 2p \rightarrow 1s$	0.3%		
$4p \rightarrow 1s$	8.0%		
$3p \rightarrow 1s$	21.2%		
$2\dot{p} \rightarrow 1s$	66.1%		
*	70		

<sup>&</sup>lt;sup>10</sup> H. A. Bethe and E. E. Salpeter, Handbuch der Physik, edited by S. Flügge (Springer-Verlag, Berlin, 1957).

<sup>&</sup>lt;sup>8</sup> J. J. Thomson, Phil. Mag. 23, 449 (1912).
<sup>9</sup> N. Bohr, Phil. Mag. 24, 10 (1913); 30, 581 (1915).

TABLE III. Three-body recombination rates  $(cm^{-3} sec^{-1})$ .  $\theta = 1000^{\circ}K$ .

	$n_e  (\mathrm{cm}^{-3})$						
n	$1 \times 10^{12}$	$2 \times 10^{12}$	$5 \times 10^{12}$	1×1013			
3	$0.1 \times 10^{12}$	$0.1 \times 10^{13}$	$0.2 \times 10^{14}$	0.1×1015			
4	$0.7 \times 10^{12}$	$0.6 \times 10^{13}$	$0.9 \times 10^{14}$	$0.7 \times 10^{15}$			
5	$2.8 \times 10^{12}$	$2.2 \times 10^{13}$	$3.5 \times 10^{14}$	$2.8 \times 10^{15}$			
6	$7.4 \times 10^{12}$	$5.3 \times 10^{13}$	$6.7 \times 10^{14}$	$4.1 \times 10^{15}$			
7	$9.0 \times 10^{12}$	$4.6 \times 10^{13}$	$3.9 \times 10^{14}$	$1.8 \times 10^{15}$			
8	$5.1 \times 10^{12}$	$2.3 \times 10^{13}$	$1.6 \times 10^{14}$	$0.5 \times 10^{15}$			
9	$2.9 \times 10^{12}$	$1.2 \times 10^{13}$	$0.7 \times 10^{14}$	$0.2 \times 10^{15}$			

mum contribution to the recombination rate comes from states with n around 6 or 7. For smaller n the rate of collisional captures decreases, because bigger and bigger energy exchanges are required in the collision between the two electrons. For higher n the re-ejection of the captured electron into the continuum becomes more and more probable; hence the maxima in Table III.

It is seen that increasing the electron density from  $10^{12}$  to  $10^{13}$  cm<sup>-3</sup> results in a slight decrease of the *n* of the level which gives the maximum contribution to the recombination rate. Analogous calculations have been made for values of  $\theta$  equal to  $3000^{\circ}$ K and  $10\ 000^{\circ}$ K. The corresponding data are not given here because they have a similar behavior of those of Table III.

The rates of recombination can be represented by an expression of the type  $\alpha(\theta)n^{\beta(\theta)}$ , where  $\beta(\theta)$  changes between about 2.65 and 2.40 when  $\theta$  changes between 1000°K and 10 000°K. If one writes  $\beta(\theta)=2+\gamma(\theta)$ , one can define the function  $f(n_{e,}\theta)=\alpha(\theta)n_{e}^{\gamma(\theta)}$  and compare it with the radiative recombination coefficient  $\alpha_{\rm rad}(\theta)$ . This is done in Fig. 1, for values of  $\theta$  equal to 1000°K, 3000°K, and 10 000°K. The full lines represent the function  $f(n_{e,}\theta)$ . It can be seen, for instance, that for an electron temperature of 1000°K and densities between  $10^{12}$  and  $10^{13}$  cm<sup>-3</sup> one gets an "effective" recombination coefficient from the three-body process of about 20–70 times as big as the radiative recombination coefficient.



Fig. 1.  $f(n_e,\theta)$  and  $\alpha_{rad}(\theta)$  vs electron density, for  $\theta = 1000$  °K, 3000 °K, and  $10\ 000$  °K.

#### **III. CONCLUSIONS**

In conclusion, the three-body process seems to give recombination rates about two orders of magnitude bigger than the radiative process, in the range of electron densities and temperatures in which a discrepancy of about two orders of magnitude exists between the radiative rates<sup>1,2</sup> and the experimental rates.<sup>3-5</sup> The calculations given here are for the case of a hydrogen gas but they are expected to be valid also for hydrogenic gases. The main contribution to the recombination rate comes indeed from states with n=5, 6, 7 or 8 and, for a given n, s and p states contribute very little. The effect of penetrating orbits is therefore quite unimportant.

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