SOVIET PHYSICS JETP VOLUME 34, NUMBER 6 JUNE, 1972

Recombination of Electrons in Triple Collisions in a Molecular Gas

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Submitted June 18, 1971

Zh. Eksp. Teor. Fiz. **61**, 2298–2304, (December, 1971)

A calculation is given of the electron-ion recombination coefficient for a gas. An allowance is made for the interaction between the electrons and the translational, rotational, and vibrational motion of the molecules.

THE limiting stage of the impact recombination process

$$A^+ + e + M \to A + M$$

in low-temperature plasma is the finite motion of a weakly bound electron in the Coulomb field of the atomic core. The rate of change in the electron energy during such motion is independent of the actual structure of the energy spectrum of the atom and is determined by gas-kinetic parameters which describe collisions of the electron with a third particle M.

A self-consistent theory of impact recombination was developed by Pitaevskiĭ.[1] The relaxation of the energy of a weakly bound electron in collisions with a third particle (a neutral atom) is regarded in[1] as the diffusion in the energy space. This basic idea has been used later in many investigations involving calculation of the recombination coefficient. In particular, the influence of electron-electron collisions has been considered by Gurevich and Pitaevskiĭ.[2] The rotation of molecules has been allowed for by Dalidchik and Sayasov.[3,4]

It is now common knowledge that electrons exchange energy very rapidly with the vibrational degrees of freedom of molecules.[5-7] This happens because an electron which is captured rapidly by a molecule alters the oscillator parameters so that the original vibrational state is no longer stationary under new conditions. The resultant negative ion dissociates into an electron and a molecule in a different vibrational state. This interaction has been considered by Schulz et al.,[8,9] who obtained the cross sections for this process in various gases.

The purpose of the present paper is to consider the influence of the same process on the coefficient of recombination in a dense low-temperature plasma.

An electron moving in a finite orbit in the field of an ion diffuses between bound states under the influence of impacts with a third particle. This third particle may be a neutral atom, a molecule, an ion, or an electron. We shall consider the case of weak ionization so that collisions with electrons and ions can be ignored.[1,2] It is shown in[3] that under some conditions an electron in a finite orbit may collide inelastically with a molecule and such collisions may excite rotational states. This excitation has a strong influence on the recombination coefficient and should be allowed for, together with the effects of elastic collisions. In addition to the processes responsible for the diffusion of electrons in the energy space, we shall also make allowance for collisions with molecules which result in a change in the vibrational states. In this case an electron in a finite orbit loses a very large energy $\Delta\epsilon \geq \hbar\omega$ and drops to lower levels where radiative transitions predominate. Electrons that undergo such collisions do not participate in diffusion and are rapidly de-excited to the ground state. Therefore, we can ignore the reverse processes involving electron transitions from deep levels to the region where diffusion over highly excited states is possible. On the other hand, if the radiative recombination begins to predominate at binding energies of the order of $\hbar\omega$, the diffusion theory can be used if $T \ll \hbar\omega$. We shall assume that this condition is satisfied. Electrons in finite orbits can also be lost from the diffusion flux by acquiring several quanta $\hbar\omega$ from molecules and going over to the continuous spectrum. The reverse process consists of a collision between an electron in an infinite orbit and a molecule in the field of an ion, which results in a transition of the electron to a bound state. The net rate of these processes is zero if the electron distribution is in equilibrium. The stationary distribution function which is obtained in the solution of the diffusion problem (see, for example,[10]) at low negative energies is close to the equilibrium distribution. Therefore, the aforementioned mutually converse nondiffusion electron transitions compensate each other almost completely. Moreover, the frequencies of electron transitions from the continuous spectrum to bound states with energies $|\epsilon| \lesssim T$ are inversely proportional to $\exp(-\hbar\omega/T)$ and the effective cross sections of these processes do not differ greatly from the cross sections for transitions of weakly bound electrons to the range of high negative energies. It follows from this discussion that we can ignore the influence of transitions from the continuous spectrum on the diffusion of electrons at energies $0 > \epsilon \gtrsim -T$.

The frequency of transitions from the continuous spectrum to the range of bound states $|\epsilon| \sim \hbar\omega$ is not generally low [it does not contain the factor $\exp(-\hbar\omega/T)$] but in this range atoms are rapidly de-excited by the radiative processes and therefore these nondiffusion transitions do not have any significant influence on the diffusion flux at low binding energies $|\epsilon| \sim T$. Nevertheless, these transitions contribute to recombination, which can be called direct recombination because it is associated with electron transitions from the continuous spectrum directly to a finite orbit characterized by a large binding energy, a high probability of emission of radiation, and negligible diffusion.

We shall calculate first the recombination coefficient associated with the diffusion flux. When an allowance is made for all the points mentioned in the preceding paragraphs, the diffusion-approximation form of the transport equation of an electron moving in a finite orbit around an ion is:

$$\dot{f}=\frac{1}{\varphi(\varepsilon)}\frac{\partial}{\partial\varepsilon}\left[\frac{\varphi(\varepsilon)}{2}(\overline{\Delta E_{ea}{}^{2}}+\overline{\Delta E_{e\text{M}}{}^{2}}+\overline{\Delta E_{ej}{}^{2}})\left(\frac{\partial f}{\partial\varepsilon}+\frac{f}{T}\right)\right]-\langle\sigma v n_{\text{M}}\rangle f. \tag{1}$$

Here, $\varphi(\epsilon)$ is the density of electron levels in the Coulomb field of the ion, given by

$$2^{1/2}\pi^{3}e^{6}m^{3/2}|\varepsilon|^{-5/2},$$

e and m are the electron charge and mass, n_M is the number of molecules in 1 cm^3, $\overline{\Delta E^2_{ea}}$ is the mean-square value of the energy losses per unit time suffered by a finite-orbit electron in elastic collisions with atoms. The corresponding diffusion coefficient $2^{-1}\varphi\,\overline{\Delta E^2_{ea}}$ is[1]

$$128\pi^{2}e^{6}m^{2}\sigma_{ea}Tn_{a}/3M_{a}|\varepsilon|. \tag{2}$$

Here, σ_{ea} is the cross section for the elastic scattering of electrons by atoms, M_a and n_a is the atomic mass and the number of atoms per 1 cm^3, $\overline{\Delta E^2_{eM}}$ and ΔE^2_{ej} are the corresponding quantities for elastic collisions of a finite-orbit electron with molecules and for collisions resulting in the excitation of the rotational states. The second diffusion coefficient in Eq. (1) is analogous to Eq. (2) except that the index "a" should be replaced with "M". According to[5], the third diffusion coefficient for nonpolar molecules (only these molecules will be considered) is[1)]

$$512\pi^{3}e^{6}mQ^{2}a_{0}^{2}n_{\text{M}}BT/45|\varepsilon|^{2}. \tag{3}$$

Here, Q is the quadrupole moment of the molecule in units of ea_0^2, a_0 is the Bohr radius, $B = \hbar^2/2I$, I is the moment of inertia of the molecule. The last terms in the transport equation $\langle\sigma v n_M\rangle$, is the average frequency of collisions between a finite-orbit electron and molecules, which result in the transfer of the molecules to higher vibrational levels. The angular brackets represent averaging over the electron distribution function, which is of the form

$$\frac{1}{\varphi(\varepsilon)}\delta\left(\varepsilon-\frac{p^{2}}{2m}+\frac{e^{2}}{r}\right), \tag{4}$$

where $\sigma(\epsilon)$ is the total cross section for the excitation of the vibrational states of a molecule by an electron, as given by Schulz. The characteristic dependences of σ on the energy of the incident electron are given, for example, in[11]. If we assume that the interaction is instantaneous,[2)] so that σ depends on the kinetic energy of the finite-orbit electron, we can find the average frequency of collisions with the aid of Eq. (4):

$$\langle\sigma v n_{\text{M}}\rangle=\frac{32\pi^{2}me^{6}n_{\text{M}}}{\varphi(\varepsilon)}\int_{0}^{\infty}\frac{\sigma(x)x}{(x+|\varepsilon|)^{4}}dx. \tag{5}$$

The integral in Eq. (5) can be represented in the form $\epsilon^*\sigma_0\Delta/(\epsilon^* + |\epsilon|)^4$, where ϵ^* is the energy at which the cross section has its maximum value, $\sigma_0 = \sigma(\epsilon^*)$, and Δ is the resonance width. A typical value of ϵ^* is of the order of several electron-volts.[11] Since the range of energies of importance to us is $|\epsilon| < \hbar\omega$, it follows that the dependence of the collision frequency on the energy of the finite-orbit electron can be ignored so that we obtain

$$\langle\sigma v n_{\text{M}}\rangle=\frac{32\pi^{2}me^{6}n_{\text{M}}\sigma_{0}\Delta}{\varphi(\varepsilon)\varepsilon^{*3}}. \tag{6}$$

The diffusion recombination coefficient can be calculated if we find the stationary solution of Eq. (1) subject to the boundary conditions

$$\begin{gathered} f(\varepsilon)=(2\pi mT)^{-3/2}e^{-\varepsilon/T},\quad \varepsilon\to 0,\\ f(\varepsilon_{0})=0,\quad |\varepsilon_{0}|\gg T. \end{gathered} \tag{7}$$

The electron distribution function can be assumed to be Maxwellian if $\epsilon = 0$ because at this energy the diffusion coefficients become infinite and the last term in Eq. (1) is finite. The second boundary condition represents the fact that in the range of high negative energies an electron becomes rapidly deactivated by losing energy through emission of radiation. The required recombination coefficient is simply equal to the diffusion flux for $|\epsilon| \to 0$, which corresponds to the stationary solution of the formulated problem.

We shall integrate Eq. (1) in two limiting cases. In the first case we shall ignore the interaction between a finite-orbit electron and the rotational degrees of freedom of a molecule. This means that the treatment corresponds either to small admixtures of a molecular gas in a monatomic environment or to a molecular gas at sufficiently high temperatures such that the rotational motion becomes unimportant. These conditions are described by the inequality[3]

$$\frac{4\pi}{15}\frac{M_{\text{M}}}{m}\frac{B}{T}\frac{Q^{2}a_{0}^{2}n_{\text{M}}}{M_{\text{M}}}\left(\frac{\sigma_{ea}n_{a}}{M_{a}}+\frac{\sigma_{e\text{M}}n_{\text{M}}}{M_{\text{M}}}\right)^{-1}\ll 1. \tag{8}$$

In the second case we shall adopt the reverse approach and ignore elastic collisions of a finite-orbit electron with atoms and molecules. This simplification is justified at sufficiently low temperatures when the converse of the inequality (8) is satisfied.

Let us consider the first case in greater detail. We shall introduce a dimensionless variable $x = |\epsilon|/T$. The distribution function of finite-orbit electrons satisfies the equation

$$\begin{gathered} \frac{d}{dx}\left[\frac{1}{x}\left(\frac{df}{dx}-f\right)\right]-\gamma_{1}f=0,\\ \gamma_{1}=\frac{3}{4}\left(\frac{T}{\varepsilon^{*}}\right)^{2}\frac{\Delta}{\varepsilon^{*}}\frac{M_{\text{M}}}{m}\frac{\sigma_{0}n_{\text{M}}}{M_{\text{M}}}\left(\frac{\sigma_{ea}n_{a}}{M_{a}}+\frac{\sigma_{e\text{M}}n_{\text{M}}}{M_{\text{M}}}\right)^{-1} \end{gathered} \tag{9}$$

subject to the boundary conditions given by Eq. (7). We shall introduce a new function

$$y(x)=\frac{\varphi(x)}{2T}(\overline{\Delta E_{ea}{}^{2}}+\overline{\Delta E_{e\text{M}}{}^{2}})\left(\frac{df}{dx}-f\right), \tag{10}$$

which obviously represents the diffusion flux of electrons. Using Eq. (9), we obtain the following equation for this function:

$$y''(x)-y'(x)-\gamma_{1}xy(x)=0. \tag{11}$$

Substituting $y = \exp(x/2)V(x)$, $z = \gamma_1^{1/3}x + (1/4)\gamma_1^{-2/3}$, we can reduce Eq. (11) to the form

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[1)] According to[3], the numerical coefficient in Eq. (3) should be 256, which is incorrect (a numerical error has been made in the calculations).

[2)] The molecule can be regarded as immobile because the electron is lost at the same point at which it is captured.

$$V''(z) - zV(z) = 0.$$

The solution of this equation, which does not increase when $x \to +\infty$, is of the form

$$V(z) = c\sqrt{z}K_{1/3}(2z^{3/2}/3), \qquad (12)$$

where $K_{1/3}$ is the Macdonald function. The constant c is found from the boundary conditions of Eq. (7)

$$c = [(2\pi m)^{3/2}T^{7/2}J(x_0)]^{-1}, \qquad (13)$$

where

$$J(x_0) = \int_0^{x_0} xe^{-x/2}[z(x)]^{1/2}K_{1/3}(2[z(x)]^{3/2}/3)\,dx.$$

Using Eqs. (10), (12), and (13), we obtain the following equation for the recombination coefficient α:

$$\alpha = y(0) = \alpha_1 K_{1/3}[(12\gamma_1)^{-1}]/2\gamma_1^{1/3}J(\infty). \qquad (14)$$

Here, α_1 is the recombination coefficient which is obtained if an allowance is made solely for the translational degrees of freedom. This coefficient is equal to[1]

$$\frac{32\sqrt{2\pi m}e^6}{3T^{5/2}}\left(\frac{\sigma_{ea}n_a}{M_a} + \frac{\sigma_{eM}n_M}{M_M}\right).$$

The integration limit x_0 in the integral $J(x_0)$ is replaced with $+\infty$ because the integrand tends to zero at large values of x. If we calculate the expression in the denominator of Eq. (14), we obtain the following final equation for the recombination coefficient:

$$\alpha = \alpha_1[6\varkappa(K_{2/3}(\varkappa)/K_{1/3}(\varkappa) - 1)]^{-1}, \ \varkappa = (12\gamma_1)^{-1}. \qquad (15)$$

In the second limiting case, when we ignore the exchange of energy between a finite-orbit electron and the translational motion of a molecule, the equation for the diffusion flux is obtained in a similar manner:

$$y''(x) - y'(x) - \gamma_2 x^2 y(x) = 0,$$

$$\gamma_2 = \frac{45}{16\pi}\frac{\sigma_0}{Q^2a_0^2}\left(\frac{T}{\varepsilon^*}\right)^3\frac{\Delta}{B}.$$

The solution of this equation is of the form

$$y(x) = ce^{x/2}D_k[(4\gamma_2)^{1/4}x], \quad k = -\frac{1}{2} - \frac{1}{8\sqrt{\gamma_2}}, \qquad (16)$$

where $D_k(x)$ is a parabolic cylindrical function. The solution increasing as $x \to +\infty$ has already been rejected. Using Eq. (16), we obtain the following expression for the recombination coefficient

$$\alpha = 2\alpha_2 D_k(0) \Big/ \int_0^\infty x^2e^{-x/2}D_k[(4\gamma_2)^{1/4}x]\,dx,$$

$$\alpha_2 = \frac{64\sqrt{2}\pi^{3/2}}{45}\frac{e^6n_M Q^2a_0^2B}{m^{1/2}T^{7/2}} \qquad (17)$$

(α_2 is the recombination coefficient which is obtained when an allowance is made solely for the molecular rotation.[3]) The integral in the denominator of Eq. (17) can be calculated analytically and the final expression for the recombination coefficient becomes

$$\alpha = \alpha_2\frac{4\gamma_2}{4\gamma_2^{1/4}\Gamma[3/4 + (16\sqrt{\gamma_2})^{-1}]/\Gamma[1/4 + (16\sqrt{\gamma_2})^{-1}] - 1}.$$

The dependences of $\Pi_1 = \alpha/\alpha_1$ on γ_1 and $\Pi_2 = \alpha/\alpha_2$ on γ_2 are plotted in Fig. 1.

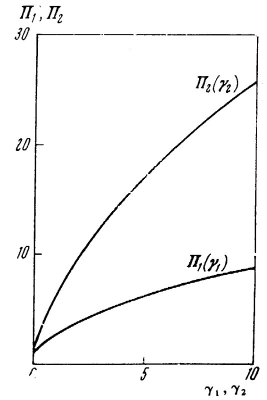

FIG. 1

The direct recombination coefficient is obviously equal to the number of collisions (per unit time) between an electron in an infinite orbit and a molecule in the field of an ion when the molecule is transferred to a higher vibrational level and the electron goes over to a finite orbit with a large binding energy $|\varepsilon| \gg T$. Since the distribution function in the continuous part of the spectrum is very nearly of the Boltzmann type and since the cross section of this collision process averaged by means of Eq. (4) does not differ greatly from Eq. (6), it follows that the direct recombination coefficient α_d is

$$(\alpha_d)_i = \alpha_i\gamma_i,$$

where i = 1 or 2, depending on which case is being considered.

We shall measure the temperature in the units

$$T^* = \frac{4\pi}{15}\frac{M_M}{m}\frac{Q^2a_0^2n_M}{M_M}\left(\frac{\sigma_{ea}n_a}{M_a} + \frac{\sigma_{eM}n_M}{M_M}\right)^{-1}B$$

and the recombination coefficient in the units $\alpha_1(T^*)$. We shall use the following notation for the relative values: $t = T/T^*$, $\tilde{\alpha} = \alpha/\alpha_1(T^*)$.

It follows from Eq. (8) that the rotation of molecules can be neglected at relative temperatures $t \gg 1$ and the total recombination coefficient $\tilde{\alpha}_r$ is then given by the expression

$$\tilde{\alpha}_r = t^{-5/2}\Pi_1(\gamma_0 t^2) + \gamma_0 t^{-1/2},$$

$$\gamma_0 = \frac{4\pi^2}{75}\left(\frac{M_M}{m}\right)^3\left(\frac{B}{\varepsilon^*}\right)^2\frac{\Delta}{\varepsilon^*}\frac{Q^4a_0^4\sigma_0n_M^3}{M_M^3} \times \left(\frac{\sigma_{ea}n_a}{M_a} + \frac{\sigma_{eM}n_M}{M_M}\right)^{-3}.$$

If $t \ll 1$, we can ignore the translational degrees of freedom of molecules and atoms and the recombination coefficient becomes

$$\tilde{\alpha}_r = 1/2\,t^{-7/2}\Pi_2(\gamma_0 t^3) + 1/2\,\gamma_0 t^{-1/2}.$$

We note that γ_1 and γ_2 expressed in the units suggested earlier can be combined into a single parameter γ_0.

Thus, the recombination coefficient is determined by two parameters γ_0 and T^*. If we know these parameters, we can calculate the recombination coefficient at all temperatures except in the vicinity of $t \sim 1$.

It is evident from Fig. 1 that the interaction of electrons with molecular vibrations enhances the recombination coefficient and this effect increases with increasing temperature. By way of example we shall consider a gas of N_2 molecules. The quantities which occur in the expressions for γ_0 and T^* have the following values for this gas:[11] $\Delta \sim 1$ eV, $\varepsilon^* = 2.3$ eV,

$B = 2.9°K$, $\sigma_0/\sigma_{eM} = 0.15$, $\sigma_{eM} = 8 \times 10^{-16}$ cm^2, $M_M/m = 5 \times 10^4$, $Q \sim 1$; hence, we find that $\gamma_0 \approx 64$ and $T^* = 6000°K$. If we use these values, we can calculate the recombination coefficient as a function of temperature. For example, at T = 1000 and 1500°K, respectively, we obtain $\gamma_2 \approx 0.3$, $\Pi_2 \approx 3.4$, and $\gamma_2 = 1$, $\Pi_2 \approx 7$, i.e., the diffusion recombination coefficient increases because of the interaction with molecular vibrations by a factor of 3.4 and 7, respectively. The direct recombination coefficient at the same temperatures represents, respectively, 0.1 and 0.14 of the diffusion coefficient.

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Translated by A. Tybulewicz
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