SOVIET PHYSICS JETP VOLUME 22, NUMBER 1 JANUARY, 1966

RECOMBINATION OF ELECTRONS IN MOLECULAR GASES

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Submitted to JETP editor February 24, 1965

J. Exptl. Theoret. Phys. (U.S.S.R.) **49**, 302-305 (July, 1965)

The electron and ion recombination coefficient in a weakly ionized gas of homopolar molecules is computed. Losses of electron energy in rotational excitation of the molecules are taken into account.

PITAEVSKIĬ [1] presented a general method of calculating the electron and ion recombination coefficients at sufficiently high pressures and not too high temperatures, when the recombination is due predominantly to triple collisions between the ion and electron with a third particle, such that the change in the electron momentum is large ($|\Delta\mathbf{p}| \sim |\mathbf{p}|$) and the change in the electron energy E is relatively small, so that the equilibrium of the electron coordinates is established much more rapidly than the equilibrium of their energies. The recombination process can then be regarded as diffusion of electrons in energy space in the direction $E < 0$, which in turn can be described by the Fokker-Planck equation. This method was used in [1] to calculate the recombination coefficient of electrons in a monatomic gas, when the collisions of the electron with the atoms are elastic.

In the case of recombination of electrons in a molecular gas, the electron colliding with the molecule can experience, besides elastic scattering, also inelastic scattering with excitation of rotational transitions of the molecule. We confine ourselves to the case of diatomic or linear homopolar molecules, the inelastic scattering of slow electrons from which was considered by Gerjuoy and Stein.[2] As shown in [2], the cross section for the rotational excitation of the molecule is much smaller than the elastic cross section, since it follows from the conservation law for the total momentum that an electron capable of producing a rotational transition should have a nonzero orbital angular momentum l either in the initial or in the final state, and at sufficiently low energies an electron with $l \neq 0$ passes far from the molecule and interacts little with it. (Upon collision with a homopolar molecule the electron interacts essentially with its quadrupole moment, so that the interaction potential decreases like r^{-3}.)

The same considerations justify the use of the first Born approximation for the calculation of the cross section of rotational excitation[1)]. Since the electron loses to the excitation of the molecule an energy of approximately $\Delta E_{\text{rot}} \sim \sqrt{B\Theta}$ where B is the rotational quantum of the molecule, $\Theta = kT$, T is the temperature of the molecular gas, and k is Boltzmann's constant (we note that if $E \sim \Theta$, then when $B \ll \Theta$ the quantity $\Delta E_{\text{rot}} \ll E$), and since the average electron energy loss in elastic collision is $\Delta E_{el} \sim 2mE/M \ll E$, we have at sufficiently low electron energies

$$\Delta E_{\text{el}} \lessapprox \Delta E_{\text{rot}}$$

Thus, when considering the recombination of electrons and ions in a molecular gas we can assume that the equilibrium of the electron coordinates is established essentially as a result of elastic collisions of the electrons with the molecules, and that the diffusion of the electrons in energy space is determined in the general case by both types of collisions.

The general scheme developed by Pitaevskiĭ [1] enables us to calculate the recombination coefficient also in this case. We shall use formulas (4), (10), and (12) from [1], which yield for the recombination coefficient α

[1)] As pointed out by E. E. Nikitin, recent more accurate calculations,[3,4] in which account was taken of the polarization interaction of the electron with the molecule and of the distortion of the plane waves that describe the electron in the initial and final states, may differ noticeably from the results of Gerjuoy and Stein. However, this difference is significant only when $\epsilon > 0.1$ eV, corresponding to a temperature $T > 1000°$, whereas we are interested in lower temperatures.

$$\alpha = \left[(2\pi m\Theta)^{3/2} \int_0^\infty e^{-\varepsilon/\Theta} \frac{d\varepsilon}{B(\varepsilon)} \right]^{-1}, \tag{1}$$

where $\epsilon = -E$ (E is the electron energy in the field of the ion, $E < 0$),

$$B(\varepsilon) = \frac{1}{2A(\varepsilon)} \left\langle \frac{\partial}{\partial t} (\Delta\varepsilon)^2 \right\rangle \tag{2}$$

($\langle \ldots \rangle$ denotes averaging),

$$A(\varepsilon) = 2^{1/2}\varepsilon^{5/2} / 2\pi^3 e^6 m^{3/2}.$$

The distribution function of the electrons in the field of the ion is of the form

$$f(p, r, \varepsilon) = A\delta\left(\frac{p^2}{2m} - \frac{e^2}{r} + \varepsilon\right).$$

In the general case, taking into account both types of collisions between the electron and the molecule, we have

$$\left\langle \frac{\partial}{\partial t} (\Delta\varepsilon)^2 \right\rangle = \left\langle \frac{\partial}{\partial t} (\Delta\varepsilon)^2_{\text{el}} \right\rangle + \left\langle \frac{\partial}{\partial t} (\Delta\varepsilon)^2_{\text{inel}} \right\rangle. \tag{3}$$

The term in (3) responsible for the elastic collisions was calculated by Pitaevskiĭ, and to calculate the term responsible for the inelastic collisions, we note that when an electron collides with a homopolar molecule in the J-th rotational state, the only molecular transitions possible are those in which the momentum J changes by ±2, so that

$$\left\langle \frac{\partial}{\partial t} (\Delta\varepsilon)^2_{\text{inel}} \right\rangle$$

$$= nB^2 \langle v[(4J+6)^2 \sigma_{J,J+2} + (4J-2)^2 \sigma_{J,J-2}] \rangle. \tag{4}$$

Here n is the number of molecules per unit volume, v the electron velocity relative to the molecule, and $\sigma_{J,J\pm2}$ is the cross section of the corresponding rotational transition.

Recognizing that in collisions with the molecule the electron can be regarded as free, we obtain for $\sigma_{J,J\pm2}$[2]:

$$\sigma_{J,J+2} = \frac{8\pi Q^2 a_0^2}{15} \left[1 - \frac{2Bm}{p^2}(4J+6)\right]^{1/2} \frac{(J+2)(J+1)}{(2J+3)(2J+1)},$$

$$\sigma_{J,J-2} = \frac{8\pi Q^2 a_0^2}{15} \left[1 + \frac{2Bm}{p^2}(4J-2)\right]^{1/2}$$

$$\times \frac{J(J-1)}{(2J-1)(2J+1)} \tag{5}$$

Here Q is the quadrupole moment of the molecule in units of ea_0^2, where a_0 is the Bohr radius.

In (4) $\langle \ldots \rangle$ denotes averaging over the electron and molecule distribution functions, i.e.,

$$\langle(\ldots)\rangle = 2A\sqrt{\frac{B}{\pi\Theta}} \int \delta\left(\frac{p^2}{2m} - \frac{e^2}{r} + \varepsilon\right)$$

$$\times\ d^3\mathbf{p}\, d^3\mathbf{r} \sum_{J=0} e^{-BJ(J+1)/\Theta} (\ldots). \tag{6}$$

Since we assume that the condition $\Theta \gg B$ is satisfied, the principal role in (6) is played by $J \gg 1$, so that summation over J can be replaced by integration with respect to J. Further, the main contribution in (1) is made by the electron energies $\epsilon \sim \Theta$, so that

$$BJm / p^2 \sim \sqrt{B/\Theta} \ll 1,$$

and therefore we can approximately write for $\sigma_{J,J\pm2}$

$$\sigma_{J,J\pm2} \approx {}^8/_{15}\pi Q^2 a_0^2 (1 + O(BJm/p^2)).$$

As a result of averaging over J we then get

$$\left\langle \frac{\partial}{\partial t} (\Delta\varepsilon)^2_{\text{inel}} \right\rangle = \frac{32\pi}{15} Q^2 a_0^2 B\Theta \frac{n}{m} \langle p \rangle, \tag{7}$$

$$\langle p \rangle = A \int d^3\mathbf{r}\, d^3\mathbf{p} \cdot p\delta\left(\frac{p^2}{2m} - \frac{e^2}{r} + \varepsilon\right). \tag{8}$$

Calculating the integral (8), we have for the mean square change in the electron energy per unit time

$$\left\langle \frac{\partial}{\partial t} (\Delta\varepsilon)^2_{\text{inel}} \right\rangle = \frac{256}{45} \pi^3 e^6 m Q^3 a_0^2 nB \frac{\Theta}{\varepsilon^2} \left(1 + O\left(\sqrt{\frac{B}{\Theta}}\right)\right). \tag{9}$$

Substituting (9) in (3) and (1) we obtain for the recombination coefficient α accurate to terms of order $\sqrt{B/\Theta}$:

$$\alpha = \alpha_0 \varphi(\Theta), \tag{10}$$

$$\alpha_0 = \frac{32\sqrt{2\pi}}{3} \frac{m^{1/2} e^6 \sigma_t n}{M\Theta^{5/2}}, \tag{11}$$

where α_0 is the recombination coefficient calculated in [1] with allowance for only elastic collisions of the electrons, and $\varphi(\Theta)$ is a certain universal function which takes into account the energy losses of the electron both by transfer of translational energy, and to rotational excitation of the molecules:

$$\varphi(\Theta) = \{1 - f(\Theta) - f^2(\Theta) e^{f(\Theta)} \operatorname{Ei}(-f(\Theta))\}^{-1},$$

$$f(\Theta) = \frac{2\pi}{15} \frac{Q^2 a_0^2}{\sigma_t} \frac{M}{m} \frac{B}{\Theta},$$

where σ_t is the total cross section for the electron-molecule collision, and Ei is the exponential integral function.

It follows from the formula that at sufficiently high temperatures when $f(\Theta) \ll 1$, the recombination coefficient coincides with that obtained by Pitaevskiĭ,[1] that is, the rotational excitation of molecules does not influence appreciably the recombination coefficient. At sufficiently small Θ, such that $f(\Theta) \gg 1$, the two highest-order terms of the asymptotic expansion of the function $\varphi(f)$ yield

$$\varphi(f) \approx {}^1/_2(f+3). \tag{13}$$

The first term f/2 in (13) corresponds to inclusion of only inelastic collisions between the electron and the molecule, and the recombination coefficient is in this case

$$\alpha = \frac{32\pi\sqrt{2\pi}}{45}\frac{Q^2a_0^2e^6n}{m^{1/2}}\frac{B}{\Theta^{7/2}}. \tag{14}$$

Formula (14), apart from a numerical factor, coincides with the elementary Thomson formula[5] where λ is the average fraction of the energy loss by the electron in rotational transitions, which according to Gerjuoy and Stein [2] is equal to

$$\alpha_T = \frac{64\sqrt{2\pi}}{81}\frac{e^6\sigma_t n}{m^{1/2}\Theta^{5/2}}\lambda, \quad \lambda = \frac{16}{15}\pi Q^2a_0^2\frac{B}{\sigma_t\bar{\varepsilon}}, \qquad \bar{\varepsilon} = \Theta.$$

A numerical calculation of the function $\varphi(f)$ shows that formula (13) is sufficiently accurate (~ 5 per cent) even when $f > 5$, thus indicating the possibility of using it in a broad temperature interval.

Formula (12) is valid if the following conditions are satisfied:

$$1)\ \Theta \ll \sqrt{m/M}e^2/a$$

(where a is the dimension of the molecule), making it possible to regard the electron as free when it collides with the molecule;

$$2)\ \Theta \gg (m/M)^{1/4}(e^2BQ^2a_0^2n)^{1/2},$$

which insures a more rapid establishment of coordinate equilibrium than energy equilibrium

$$3)\ \Theta \gg B.$$

In this case the decisive condition is 1) since conditions 2) and 3) are practically always satisfied.

In conclusion we note that the Pitaevskiĭ method employed here can be extended also to other classes of molecules, for example those having a dipole moment and small vibrational quanta.

We take the opportunity to express deep gratitude to L. P. Pitaevskiĭ for help with the work and also A. S. Kompaneets, G. K. Ivanov, and E. E. Nikitin for a discussion of the results.

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Translated by J. G. Adashko
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