

IONIZATION RATE CONSTANT AT HIGH TEMPERATURES  
AND SMALL ELECTRON CONCENTRATIONS

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We will calculate the rate constant for thermal ionization of a monatomic gas by electrons, taking into account the nonuniformity of the electron-energy distribution function. The formulation of the problem is the same as in our previous study, the only difference being that we will consider the case of small electron concentrations [1]. We have in mind electron concentrations such that the rate at which a Maxwell distribution is established for the electron gas at electron energies of the order of the ionization potential  $I$  is governed by electron-atom rather than electron-electron collisions. At this electron concentration,  $c = n_e/n_a$  (where  $n_e$  and  $n_a$  are the numbers of electrons and atoms per unit volume), the condition

$$c \ll \frac{m}{M} \frac{\sigma_{ea}(I)}{\sigma_{ee}(I)} \quad \left( \frac{\sigma_{ee}(I)}{\sigma_{ea}(I)} \approx Q \right) \quad (1)$$

should be satisfied.

Here  $m$  and  $M$  are the masses of the electron and atom,  $\sigma_{ea}(I)$  and  $\sigma_{ee}(I)$  are the cross sections of elastic scattering of electrons at atoms and electrons for an energy  $I$ , and  $Q$  is the coulombic logarithm.

The ionization rate constant is calculated as a function of the atomic temperature. The rate constant differs substantially from its equilibrium value over a broad temperature range as a result of the loss of electron energy in ionization.

**1. Formulation of Problem.** We will consider a gas with a constant heavy-particle (atom and ion) temperature  $T$  far from ionization equilibrium, so that recombination processes can be neglected. We will assume the temperature to be so high ( $T > I/20$ ) that the ionization rate is determined by the rate of the transition to the first excited atomic state. This problem was considered in detail earlier [1].

We find the electron distribution function  $f(t, \varepsilon)$  by solving the kinetic equation

$$\dot{f} = I_{ee} + I_{ea} + I_{ei} + I_i \quad (1.1)$$

where the symbols  $I_{ee}$ ,  $I_{ea}$ , and  $I_{ei}$  represent the integrals for collisions of electrons with electrons, atoms, and ions, respectively. The last term on the right side of Eq. (1.1) takes into account the ionization.

The first three collision integrals in Eq. (1.1) have the order of magnitude  $\Delta f/\tau$ , where  $\Delta f$  is the deviation of the distribution function from the equilibrium value and  $\tau$  is the energy relaxation time for the corresponding collision process. An estimate of this time is

$$\tau \sim T^2 / \langle \delta(\Delta E)^2 / \delta t \rangle$$

where  $\langle \delta(\Delta E)^2 / \delta t \rangle$  is the mean-square energy loss per unit time for the energy-exchange process in question. For electron-electron collisions, this quantity is proportional to  $\varepsilon^{-1/2}$ ; for elastic electron-atom collisions, it is proportional to  $\varepsilon^{3/2}$ , so that

$$\tau_{ee} \sim \varepsilon^{1/2}, \quad \tau_{ea} \sim \varepsilon^{-3/2} \quad (1.2)$$

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i.e., the efficiency of electron-electron collisions decreases with increasing energy, while that of electron-atom collisions increases rapidly.

Taking inequality (1) into account, electron-electron collisions at large electron energies  $\varepsilon > E_1$  ( $E_1$  is the energy of the first atomic excited state, reckoned from the ground level) can be neglected in comparison with elastic electron-atom collisions. Naturally, both types of collisions are effective when  $\varepsilon \ll E_1$  and should be taken into consideration. Equation (1) is equivalent to the inequality

$$\tau_{ee} \gg \tau_{ea}, \quad \varepsilon > E_1 \quad (1.3)$$

At small energies, the inequality

$$\tau_{ee} \ll \tau_{ea}, \quad \varepsilon \rightarrow 0 \quad (1.4)$$

is satisfied by virtue of Eq. (1.2).

For the electron-ion relaxation time  $\tau_{ei}$ , we have the inequalities

$$\tau_{ei} \gg \tau_{ea}, \quad \tau_{ei} \gg \tau_{ee} \quad (1.5)$$

which are valid for all energy regions, since  $n_i = n_e \ll n_a$  in accordance with Eq. (1) ( $n_i$  is the number of ions per unit volume), and the ion mass is  $M/m$  times the electron mass.

Inequalities (1.3) and (1.5) permit considerable simplification of the initial kinetic equation. At large energies  $\varepsilon > E_1$ , we can neglect the collision integrals  $I_{ee}$  and  $I_{ei}$ . The remaining collision integral  $I_{ea}$  can be represented in the form of a differential relationship of the Fokker-Planck type, expanding the electron distribution function under the integral (for the energy transferred during collision) and assuming that the atoms have a Maxwell distribution with temperature  $T$ . As a result, Eq. (1.1) for the energy region  $\varepsilon > E_1$  takes the form

$$f = \frac{1}{\varphi(\varepsilon)} \frac{\partial}{\partial \varepsilon} \left[ \frac{\varphi(\varepsilon)}{2} \left\langle \frac{\partial}{\partial t} (\Delta E_{ea})^2 \right\rangle \left( \frac{\partial f}{\partial \varepsilon} + \frac{f}{T} \right) \right] - \sigma_i(\varepsilon) n_a \left( \frac{2\varepsilon}{m} \right)^{1/2} f \quad (1.6)$$

$$\varphi(\varepsilon) = 4\pi m^{-3/2} (2\varepsilon)^{1/2}$$

Here  $\varphi(\varepsilon)$  is the level density, and  $\sigma_i(\varepsilon)$  is the cross section for transition of an atom from the ground level to the first level. This cross section can be approximately represented by the linear energy function

$$\sigma_i(\varepsilon) = \sigma \theta(\varepsilon - E_1) (\varepsilon - E_1) / E_1$$

Here  $\theta(x)$  is a Heavyside function. The constant  $\sigma$  depends on the specific type of atom. For most elements,  $\sigma \sim 10^{-16} \text{ cm}^2$ . Assuming the cross section of elastic electron scattering by the atoms  $\sigma_{ea}$  to be independent of energy, we find that the mean-square energy loss per unit time is

$$\langle \partial (\Delta E_{ea})^2 / \partial t \rangle = 2^{1/2} M^{-1} m^{1/2} \sigma_{ea} n_a T \varepsilon^{3/2}$$

We now introduce a distribution function normalized for a single electron,  $f = n_e f_1$ . The left side of Eq. (1.1) can be represented in the form

$$f_1 n_e + K n_e n_a f_1 \quad (1.7)$$

Here  $K$  is the ionization rate constant, defined by the integral

$$\int_{E_1}^{\infty} \sigma_i(\varepsilon) \left( \frac{2\varepsilon}{m} \right)^{1/2} f_1 \varphi d\varepsilon \quad (1.8)$$

In order to calculate the distribution function  $f_1$  at temperatures considerably below the ionization potential, it is sufficient to find the steady-state solution to the kinetic equation  $f_1' = 0$  (the so-called quasi-steady-state approximation [1]).

Because of the smallness of the ionization rate constant, which depends exponentially on temperature, the second term in Eq. (1.7) can be omitted. It exceeds the last term in Eq. (1.6), which takes account of

the ionization, only over a very narrow energy range near the excitation threshold for the first level. However, this very narrow energy interval  $\delta E$  has no effect on the trend of the solution.\* Eventually, the kinetic equation for energies  $\varepsilon > E_1$  is written in the form

$$\frac{1}{\varphi(\varepsilon)} \frac{d}{d\varepsilon} \left[ \frac{16\pi\sigma_{ea} n_a T \varepsilon^2}{mM} \left( \frac{df_1}{d\varepsilon} + \frac{f_1}{T} \right) \right] - n_a \sigma \sqrt{\frac{2}{m}} \frac{V_{\varepsilon}(\varepsilon - E_1)}{E_1} f_1 = 0 \quad (1.9)$$

The initial equation [Eq. (1.1)] can also be greatly simplified in the energy region  $\varepsilon < E_1$ . There are no nonelastic collision processes in this region and  $I_1 = 0$ . [With the high temperatures and small electron concentrations under consideration in Eq. (1), transitions from the first excited level to higher levels and in the continuous-spectrum region take place primarily by collisions between heavy particles.]

Inequality (1.5) enables us to neglect collisions between electrons and ions. By virtue of Eqs. (1.3) and (1.4), neither of the remaining collision integrals,  $I_{ee}$  and  $I_{ea}$ , can be neglected in the energy region  $\varepsilon < E_1$ . The expression for the collision integral  $I_{ea}$  in Eq. (1.9) is also applicable to low energies. The collision integral  $I_{ee}$  can also be reduced to a differential expression of the Fokker-Planck type, using the electron-flux expression obtained by Landau [2]

$$j_i = \frac{\pi e^4 Q}{m^2} \int \left( f(v) \frac{\partial f(v')}{\partial v_k} - f(v') \frac{\partial f(v)}{\partial v_k} \right) \frac{u^2 \delta_{ik} - u_i u_k}{u^3} d^3 v' \quad (1.10)$$

Here  $u_i = v_i - v_i'$  is the relative velocity vector and  $\delta_{ik}$  is the unit tensor.

In view of the fact that, as a result of the strong energy exchange between the electrons and atoms [Eq. (1)] and by virtue of Eq. (1.4), the electron distribution function  $f(\varepsilon)$  at low energies  $\varepsilon \ll T$  differs little from the equilibrium distribution function, which is a Maxwellian with the temperature  $T$ , we can represent Eq. (1.10) in the form

$$J(\varepsilon) = -8\pi^2 e^4 Q n_a m^{-2} T \left( df/d\varepsilon + f/T \right) S(\varepsilon/T) \quad (1.11)$$

where

$$S(\varepsilon/T) = 2\pi^{-1/2} \int_0^{\varepsilon/T} \sqrt{x} e^{-x} dx$$

Here  $J(\varepsilon)$  is the electron flux in the energy space. The value of  $S$  differs little from one at energies  $\varepsilon > T$  and tends to zero at low energies. However, the main role at such energies is played by collisions leading to large-angle scattering. Such collisions are neglected in the derivation of Eq. (1.11). Their precise evaluation is a complex problem, but the low-energy region is not important for our purposes, as will be seen from the discussion below. We can therefore replace the function  $S(\varepsilon/T)$  in Eq. (1.11) by one with good accuracy, so that the collision integral  $I_{ee}$  has the final form

$$\frac{1}{\varphi(\varepsilon)} \frac{\partial}{\partial \varepsilon} \left[ \frac{8\pi^2 e^4 Q n_a T}{m^2} \left( \frac{\partial f}{\partial \varepsilon} + \frac{f}{T} \right) \right]$$

For the quasisteady-state case in the energy region  $\varepsilon < E_1$ , taking all the foregoing into account, kinetic equation (1.1) has the form

$$\frac{1}{\varphi(\varepsilon)} \frac{d}{d\varepsilon} \left[ \left( \frac{8\pi^2 e^4 Q n_a T}{m^2} + \frac{16\pi\sigma_{ea} n_a T \varepsilon^2}{mM} \right) \left( \frac{df_1}{d\varepsilon} + \frac{f_1}{T} \right) \right] = 0 \quad (1.12)$$

**2. Solution of Kinetic Equation.** We will seek solutions to Eqs. (1.9) and (1.12) and combine them and their first derivatives at an energy  $\varepsilon = E_1$ . We introduce the dimensionless quantities  $x = \varepsilon/T$  and  $\beta = E_1/T$ . Using this notation, Eq. (1.9) is rewritten as

$$f_1''(x) + \left( 1 + \frac{2}{x} \right) f_1'(x) + \frac{2 - \alpha(x - \beta)}{x} f_1(x) = 0 \quad (2.1)$$

$$\alpha = M\sigma / 2m\sigma_{ea}\beta, \quad \alpha \gg 1$$

\* It can be demonstrated that  $\delta E/T \approx \sqrt{E_1/T} \exp(-E_1/T)$ .

Equation (2.1) reduces to a Whittaker equation. The solution vanishing at infinity has the form

$$Bx^{-1} \exp(-x/2) W_{p,1/2}(x\sqrt{1+4\alpha}) \quad (p = (1 + \alpha\beta)/\sqrt{1+4\alpha}) \quad (2.2)$$

Here  $W_{p,1/2}$  is a type II Whittaker function and B is the normalization constant. When the influence of ionization is neglected, Eq. (2.2) becomes a Maxwellian. For this purpose, it is necessary to set the parameter  $\alpha$  equal to zero.

Let us now find the distribution function in the energy region  $\varepsilon < E_1$ . We are seeking a solution in the form

$$f_1(\varepsilon) = (m/2\pi T)^{3/2} (1 + g(\varepsilon)) \exp(-\varepsilon/T) \quad (2.3)$$

with the boundary conditions

$$g(0) = 0, \quad g(E_1) = \text{const} \neq 0$$

Substituting Eq. (2.3) into Eq. (1.12), we obtain

$$\frac{d}{d\varepsilon} [(\varepsilon_0^2 + \varepsilon^2) \exp(-\frac{\varepsilon}{T}) \frac{dg}{d\varepsilon}] = 0 \quad (\varepsilon_0 = (\frac{\pi Q e^4 c m}{2M \sigma_{ea}})^{1/2})$$

The integral of this equation, taking into account the boundary conditions, has the form

$$g(\varepsilon) = -C_1 \int_0^\varepsilon (\varepsilon_0^2 + \varepsilon^2)^{-1} \exp\frac{\varepsilon}{T} d\varepsilon$$

The continuity condition for the distribution function and its first derivative at the point  $\varepsilon = E_1$  yields the following expressions for the constants B and  $C_1$ :

$$\begin{aligned} B &= (m/2\pi T)^{3/2} e^{-\beta} F' [\Phi(F' - F/T) - F\Phi']^{-1} \\ C_1 &= -(\Phi' + \Phi/T) [\Phi(F' - F/T) - F\Phi']^{-1} \end{aligned} \quad (2.4)$$

We introduce the notation

$$F(\varepsilon) = \int_0^\varepsilon (\varepsilon_0^2 + x^2)^{-1} \exp\frac{x}{T} dx \quad (2.5)$$

$$\Phi(\varepsilon) = T\varepsilon^{-1} \exp(-\varepsilon/2T) W_{p,1/2}(\varepsilon T^{-1} \sqrt{1+4\alpha}) \quad (2.6)$$

The derivatives and functions in Eqs. (2.5) and (2.6) are taken for the point  $\varepsilon = E_1$  in Eq. (2.4). It follows from the form of Eq. (2.5) that the value of the function  $F(\varepsilon)$  at high energies  $\varepsilon > T$  and specifically at  $\varepsilon = E_1$  is governed principally by the magnitude of the expression under the integral in the vicinity of the upper limit of integration. In this region, the function  $S(\varepsilon/T)$ , defined by Eq. (1.11), equals one for all practical purposes.

The function  $F(\varepsilon)$  can be calculated with any desired degree of accuracy by integrating Eq. (2.5) by parts. Using this method, we obtain

$$F(E_1) = (\varepsilon_0^2 + E_1^2)^{-1} T e^\beta [1 + 2E_1 T (\varepsilon_0^2 + E_1^2)^{-1} + O(\beta^{-2})] \quad (2.7)$$

The derivative  $\Phi'(E_1)$  is calculated with the Whittaker-function asymptotic [3]

$$W_{p,1/2}(y) = \frac{\Gamma(1/3)}{\sqrt{\pi}} \left(\frac{y}{6}\right)^{1/6} \exp[p(\ln p - 1)] \left[1 - \frac{\Gamma(5/6)}{2\sqrt{\pi}} \frac{y-4p}{(y/3)^{1/2}} + O\left(\frac{6(y-4p)}{y}\right)\right] \quad (2.8)$$

which is valid when

$$y \sim 4p, \quad y - 4p = o[(y/6)^{1/6}]$$

The first condition is always satisfied in the case under consideration, while the second leads to the inequality

$$\left(\left(\frac{3}{2}\right)^{1/2} \frac{m}{M} \frac{\sigma_{ea}}{\sigma} \beta^2\right)^{1/2} \ll 1$$

which imposes an unimportant limitation on the lower end of the temperature region with which we are dealing.

We use Eqs. (2.7) and (2.8) to find the constants B and  $C_1$

$$B = \left(\frac{m}{2\pi T}\right)^{1/2} \beta e^{-\beta/2} \left\{ W_{p, 1/2}(\beta \sqrt{1+4\alpha}) \left[ \frac{1}{2} + \frac{\Gamma(5/6)}{\sqrt{\pi}} \left(\frac{3\alpha}{2\beta}\right)^{1/2} + O(\beta^{-1}) \right] \right\}^{-1}$$

$$C_1 = F(E_1)^{-1} \left\{ 1 - \left[ \frac{1}{2} + \frac{\Gamma(5/6)}{\sqrt{\pi}} \left(\frac{3\alpha}{2\beta}\right)^{1/2} + O(\beta^{-1}) \right]^{-1} \right\}$$
(2.9)

It can be seen from the latter expression that the influence of ionization on the distribution function becomes quite substantial for small concentrations, this influence being noticeable at energies  $\epsilon < E_1$ . This phenomenon makes it necessary to reduce the normalization factor B by the factor in brackets in Eq. (2.9), which can be neglected at large concentrations [1].

3. Calculation of Ionization Rate Constant. The ionization rate constant in Eq. (1.8) is most easily calculated with the aid of Eq. (1.9), which must be multiplied by  $\varphi(\epsilon)$  and integrated from  $E_1$  to  $\infty$ . This yields

$$K = - \frac{16\pi\sigma_{ea} T E_1^2}{mM} \left( \frac{df_1}{d\epsilon} + \frac{f_1}{T} \right) \Big|_{\epsilon=E_1}$$

Substituting in the distribution-function expressions in Eqs. (2.2) and (2.4), we obtain

$$K = - \frac{8\sigma_{ea} E_1^2 \sqrt{m} e^{-\beta}}{\sqrt{2\pi} M \sqrt{T}} \frac{F'(\Phi' + \Phi/T)}{-F\Phi' + \Phi(F' - F/T)}$$

Using Eqs. (2.9) and (2.10), we find the final expression for the ionization rate constant

$$K = \frac{8\sigma_{ea} E_1^2 \sqrt{m} e^{-\beta}}{\sqrt{2\pi} M T^{3/2}} \left( 1 - \left[ \frac{1}{2} + \frac{\Gamma(5/6)}{\sqrt{\pi}} \left(\frac{3\alpha}{2\beta}\right)^{1/2} \right]^{-1} \right) \left( 1 + \frac{2E_1 T}{\epsilon_0^2 + E_1^2} \right)^{-1}$$

It is of interest to compare this result with that obtained when the influence of ionization on the distribution function is neglected. Designating the corresponding ionization rate constant as  $K_0$ , we find for the ratio  $K/K_0$

$$\frac{\beta}{\alpha} \left( \frac{\beta}{\beta+2} \right) \left[ 1 - \left( \frac{1}{2} + \frac{\Gamma(5/6)}{\sqrt{\pi}} \left(\frac{3\alpha}{2\beta}\right)^{1/2} \right)^{-1} \right] \left( 1 + \frac{2E_1 T}{\epsilon_0^2 + E_1^2} \right)^{-1}$$
(3.1)

Equation (3.1) is essentially an expansion of  $K/K_0$  for the small parameters  $\beta\alpha^{-1}$  and  $\beta^{-1}$ . The last three terms are only small corrections in the temperature region under consideration. The principal term in the expansion of  $K/K_0$  for these parameters is therefore

$$\frac{\beta}{\alpha} = 1.1 \cdot 10^{-3} \frac{\sigma_{ea}}{\sigma} A^{-1} \beta^2$$
(3.2)

where A is the atomic weight of the gas in question. The value of Eq. (3.2) over the temperature region under consideration ( $\beta < 20E_1/I$ ) is considerably less than one for all gases.

#### LITERATURE CITED

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