ON THE THEORY OF IONIZATION AND RECOMBINATION IN A LOW-TEMPERATURE PLASMA

L. M. BIBERMAN, V. S. VOROB'EV, and I. T. YAKUBOV

Institute of High Temperatures, U.S.S.R. Academy of Sciences

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Expressions for the recombination and ionization rates in a plasma of arbitrary composition are obtained on basis of the concept of the two processes being one of electron diffusion in discrete energy space. Electron-atom collisions and radiative processes are taken into account. The possible absence of Maxwellian energy distribution of free electrons is taken into account. Results of concrete calculations are presented and compared with the experiments.

The kinetics of ionization and recombination in a partially ionized plasma has a number of distinguishing features, which are closely connected with the multi-level structure of the atoms and molecules. The recombining electron, before producing an atom in the ground state, passes through a set of excitation states. The recombination rate is determined by the time of passage through these states, and is therefore closely connected with the distribution of the atoms over the energy levels. In final analysis, the recombination rate is a complicated function of the concentration of the light and heavy particles, their energy distributions (the Maxwellian electron energy distribution may be violated), and by the condition for the yield of the radiation. All the foregoing applies equally well to ionization.

The rates of ionization and recombination are customarily represented as the product of the electron density, raised to a certain power, and an appropriate coefficient. However, owing to the dependence of these coefficients on a number of parameters, it is preferable to speak of ionization and recombination functions (IF and RF). The IF and RF can be determined by solving a system of balance equations written out for each of the excited states of the atom. This system should be solved simultaneously with the kinetic equation for the electrons.

Starting with the work of Bates and co-workers, a numerical method of solving this problem has gained wide acceptance, and has made it possible to compile tables of IF and RF for certain elements and for a limited range of parameters. It is important, however, that the electron energy distribution was assumed to be Maxwellian, and the emission yield was considered only in two limiting cases.

On the other hand, it was noted that although the levels in the atoms are not equidistantly located, the probabilities of the transitions between the energetically close levels are the largest. In this case, the recombination can be regarded as a certain slow probabilistic process of the Brownian-motion type in energy space, and a suitable Fokker-Planck equation can be written, with the discrete spectrum replaced by a continuous energy. The latter circumstance has narrowed down the limits of applicability of the indicated approach.

In this paper we use a modified diffusion approximation, in which the real discrete structure of the energy spectrum is retained. This calls for the derivation and solution of a corresponding Fokker-Planck finite-difference equation. Account is taken of the collision and radiative processes. It is assumed that the Maxwellian distribution for the electrons is violated. Allowance for the discreteness makes it possible to consider not only recombination but also ionization, and the limits of the analysis of recombination in this case are greatly broadened. General expressions are obtained for the IF and RF, as well as approximation formulas. The connection between the IF and RF is discussed. Results of calculations are presented for a number of atoms and are compared with the experimental data.

FUNDAMENTAL EQUATIONS

We write the rate of change of the electron concentration in the form

$$\frac{dn_e}{dt} = n_e n_\beta - n_e^2 - VJ, \quad (1)$$

where $\beta$ and $\alpha$ are functions of the ionization and recombination, $VJ$ takes into account the transport phenomena. We are interested below only in volume processes ($\alpha$ and $\beta$).

The functions $\alpha$ and $\beta$ should be determined from the solution of the system of nonstationary particle-balance equations for each of the levels of the atom. However, the problem can be greatly simplified by using the condition that the excited states are quasistationary. The point is, that in a wide range of conditions, the following conditions are satisfied in the plasma

$$\sum_{\kappa} n_k \approx n_{\alpha} n_{\beta} \quad (n_k - concentration of the atoms in the state k).$$

Then the concentration of the atoms in the excited states will...

1) The balance equation follows, under certain assumptions, from a more rigorous analysis of this problem, see, for example, [1-2]. Among the latest papers, mention should be made of [3].

2) The recombination rate is sometimes assumed equal to $\alpha^* n_k^2$. Then $\alpha^* = n_\kappa n_{\beta}$. 

1070
have time to adjust itself to relatively slow changes of \( n_0 \) and \( n_1 \).

The problem can be solved quantitatively by comparing the ionization relaxation time \( \tau_{10} \) and the relaxation time \( \tau_k \) of the individual excited states. Estimates performed in \(^{1,11}\) have shown that \( \tau_{10} \gg \tau_k \) (k \( \approx \) 2) in a wide range of conditions. It is clear that when \( \tau \gg \tau_k \) it is possible to use the quasi-stationarity approximation. Quasi-stationarity means that at each given instant of time, in all cross sections of energy space, there is one and the same particle flux \( j_k \) which determines the IF and RF. The assumption of quasi-stationary development of ionization or recombination makes it possible to calculate \( j_k \) in the stationary approximation.

In \(^{1,11}\) we investigated the distribution of the atoms over the levels and of the electrons over the energies in a stationary nonequilibrium plasma. The processes in the discrete energy spectrum were described with the aid of a Fokker-Planck finite-difference equation. The processes in the energy continuum were described with the aid of a differential Fokker-Planck equation. Account was taken of the influence of the inelastic electron-atom collisions on the free-electron distribution, as well as of the reaction of the non-Maxwellian behavior on the distribution over the excited states. It turned out that the final results can be represented in the form of formulas that are obtained when account is taken of only transitions between neighboring energy levels (the single-quantum approximation). However, the probabilities of these transitions differ from the single-quantum ones and are expressed in terms of moments that are characteristic of the diffusion approximation. Thus, for the transition \( k \rightarrow k + 1 \), this effective probability is given by

\[
\langle z_{k+1} \rangle = \left( E_k - E_{k+1} \right)^{-1} \sum_{\text{n}} \langle w_{k,n} \rangle \left( E_n - E_k \right) \left( E_n - E_{k+1} \right),
\]

where \( \langle w_{k,n} \rangle \) is the probability of the \( k \rightarrow n \) transition, averaged over the free-electron distribution. It is easy to see that \( \langle z_{k,K_{k+1}} \rangle = \langle w_{k,K_{k+1}} \rangle \) on going over to the single-quantum approximation, and this quantity is proportional to the mean square of the energy transferred by the electrons to the atoms on going over to a quasi-continuous energy change.

Moments of the type (2) can be calculated with the aid of the sum rules, making it possible to represent \( \langle z_{k,K_{k+1}} \rangle^{(0)} \) in the form

\[
\langle z_{k,K_{k+1}} \rangle^{(0)} = n_k \frac{4 \sqrt{2} \pi e^2 A_k}{\Delta E_k \sqrt{m T_e}} \exp \left( -\frac{\Delta E_k}{T_e} \right), \quad \Delta E_k = E_k - E_{k+1},
\]

\[
\langle z_{k,K_{k+1}} \rangle^{(2)} = n_k \frac{4 \sqrt{2} \pi e^2 A_k^2 \Delta E_k}{\Delta E_k (E_k - E_{k+1}) \sqrt{m T_e}} \exp \left( -\frac{\Delta E_k}{T_e} \right), \quad k \geq 2,
\]

where \( \langle \cdot \rangle \) denotes averaging over the Maxwellian electron-energy distribution, and \( A_k \) is the so-called Coulomb logarithm for the bound states, a plot of which against \( \Delta E_k/T_e \) is shown in Fig. 1.

In the absence of strong external fields, the main factor violating the Maxwellian distribution may be the inelastic collisions with the nonuniformly populated atoms. This process is most appreciable in the high-energy region, where the frequency of the Maxwellizing collisions may turn out to be insufficient. Formally this circumstance can be taken into account by replacing \( \langle z_{12} \rangle \) by \( \langle z_{12} \rangle \cdot F \), where

\[
F = \frac{1 + (4 e^2 - 1)}{c (1 + 4 e^2 + 1)} = \frac{n_k \langle z_{12} \rangle}{n_e \langle z_{12} \rangle},
\]

\[
\langle z_{12} \rangle = \frac{2 \sqrt{2} \pi e^2}{T_e m T_e} \exp \left( -\frac{\Delta E_1}{T_e} \right),
\]

\( \lambda \) is the Coulomb logarithm for the interelectronic collisions; these collisions are usually the main Maxwellizing factor.\(^{12}\) For \( k \geq 2 \) we assume \( \langle z_{k,k+1} \rangle = \langle z_{k,k+1} \rangle^2 \).

The motion of the bound electron over the energy spectrum, resulting from the radiation acts, is a directional character and does not constitute diffusion. In the section of energy space between the levels \( k \) and \( k + 1 \), the flux due to the radiation processes can be approximately written in the form

\[
n_k n_{k+1} = \sum_{i=0}^{n_e} \sum_{\text{n-n}} \alpha_n, \quad \sum_{n=0}^{n_e} \sum_{\text{n-n}} \alpha_n,
\]

where \( \alpha_n \) is the probability of the spontaneous transition \( i \rightarrow n \), and \( \alpha_{nk} \) is the probability of radiative recombination at the level \( k \). It can be shown from (5) that for each level \( k \) the transitions \( k - 1 \) (\( i < k \)), \( k + 1 \rightarrow k \), and the radiative recombination have been taken into account accurately. In the presence of reabsorption, \( \alpha_n \) in (5) is replaced by \( \alpha_n = \alpha_n \theta_n \), where \( \theta_n \) is the probability that the given photon will leave the plasma without absorption.\(^{12}\)

Writing now the expression for the total flux \( j_k \) in the section of energy space between each pair of levels, we obtain the following system of coupled equations:

\[
j_k = n_k (\langle z_{k,k+1} \rangle - n_{k+1} \langle z_{k+1,k} \rangle + \alpha_{nk} - n_k \alpha_{nk}).
\]

Solving the equations and connecting the populations of the last of the discrete levels realized in the plasma with the electron concentration, we obtain expressions for the IF and RF:\(^{21}\)

\[
\beta = n_k K_{k+1} \sum_{k=1}^{n_e} S_k \left( 1 + \frac{n_k}{\sum_{k=1}^{n_e} S_k} \right)^{-1} \alpha \left( \sum_{k=1}^{n_e} S_k \right)^{-1} ;
\]

\[
\Pi_k = K_k = \sum_{k=1}^{n_e} \left( \langle z_{k,k+1} \rangle \right)^{-1} \sum_{n=0}^{n_e} \langle z_{k,n} \rangle \sum_{k=1}^{n_e} S_k \left( 1 + \frac{n_k}{\sum_{k=1}^{n_e} S_k} \right)^{-1} \alpha \left( \sum_{k=1}^{n_e} S_k \right)^{-1} ;
\]

\( \Pi_k \) is a factor that takes into account the influence of the radiation yield on the population of the \( k = 1, \ldots, n_e \)-st
level. \( \Sigma_l \) is the partition function of the ion, and \( g_k \) is
the statistical weight of the level \( k \). The energy \( E_k \) is reckoned from
the continuum, \( n = n_e + \sum_{k \geq 1} n_k \) is the total number of heavy
particles.

This leads to a general relation between the IF and RF:

\[
\beta = a K n^l \left( 1 + \sum_{\lambda > 1} a_\lambda \frac{\partial \lambda}{\partial \epsilon} \right)^{-1}.
\]

(8)

IONIZATION BY ELECTRON IMPACT AND THREE-PARTICLE RECOMBINATION

If radiative processes can be neglected, then

\[
a = \left( \frac{\sum n_k E_k}{\sum n_k E_k^l} \right)^{-1}. \quad \beta = a K n.
\]

(9)

The detailed-balancing relation \( \beta = a K n \) is valid also
in the absence of the atoms over the excited states. (10) The highly-excited
levels are in relative equilibrium with the continuum. The low-lying levels are close to equilibrium with the
ground state. Obviously, upon ionization (recombination), the bound electron rapidly passes through energy
intervals corresponding to these groups of levels. As to the group of intermediate essentially-nonequilibrium
states, it constitutes the "bottleneck" for the flux in energy space. The passage through the bottleneck in fact
determines the rate of the ionization (recombination).

The position of the bottleneck \( E^* \) can be estimated by
using the approximate expression for the populations, obtained earlier in (11), referred to the equilibrium values
of \( T_e \). \( y_k = n_k / n_0^k, y_e = n_e / n_0^e \):

\[
y(E_k) = y(E_l)(\frac{E_l}{T_e}) + \mu(E)\left[ \frac{E_l}{T_e} - \frac{E_k}{T_e} \right].
\]

(10)

From the condition \( \alpha q_y / 2 E^* = 0 \) it follows that \( E^* = 3 T_e \). The lower limit of the bottleneck can be identified with the point where the derivative \( \alpha q_y / 2 E \) decreases by a factor \( e \); this yields a value \( \sim 7 T_e / 2 \).

A. Low temperatures. The bottleneck falls is the region of strongly excited states, in which the discrete-
ness of the levels can be neglected. Going over in (9) from summation to integration, and assuming the ex-
acted states to be hydrogen-like, we obtain

\[
\alpha^* = \frac{3 n_0^e n_0^l}{2 \hbar^2 a^3} \frac{E_l}{T_e}\left( \frac{E_l}{T_e} \right)^l.
\]

(11)

\( \Lambda \) is the value of the \( \Lambda_k \) in the region of the bottleneck. We can assume

\( \Lambda \approx 0.2; R_y = e^l m^l / 2 \hbar^2 \).

The formula of the type (11) was obtained earlier in (12), where the discreteness of the levels was neglected
from the very outset. By stipulating that the difference between the neighboring levels in the bottleneck zone
be smaller than \( T_e \), we can readily obtain a criterion for the validity of (11):

\[
2(\gamma_l)^l / T_e = R_y \ll 1.
\]

It is important that (11) does not depend on the type of
the atom. This is due to the fact that the rate of the
recombination (ionization) is determined by the passage
through the highly-excited hydrogen-like states.

B. High temperatures. The bottleneck is located in the
energy interval \( (E_1 - E_2) \). Retaining in (9) only the
first term, we obtain

\[
a = \frac{h^2 \mu \Lambda_1}{2 \pi n_0^l \mu_1 \mu_2} \exp \left( \frac{E_2}{T_e} \right) \exp \left( \frac{E_1}{T_e} \right) \left( \Lambda_1 \right)^{-1} \ll 1.
\]

(12)

Formula (12) for \( \beta \) corresponds to the approximation of "immediate ionization" of the excited atoms that
appear during the course of the relaxation. The ionization
rate is determined by the excitation rate. A criterion
for the applicability of (12) is the inequality \( S_k \gg \sum S_k \). Calculating \( \sum S_k \) in the quasicontinuous
approximation, we can write this inequality in the form

\[
2 A \frac{\Delta E_1}{3 \Lambda_1 T_e} \exp \left( \frac{E_2}{T_e} \right) \left( \Lambda_1 \right)^{-1} \ll 1.
\]

(13)

If it follows from (12) that when \( F_0 \neq 1 \) the IF and RF depend not only on the temperature but also on \( a_{n_0} \). In
the limit of a strong non-Maxwellian distribution (\( F_0 < 1 \)), \( \beta \) is determined by the rate of the interelectron
collisions for an electron with energy \( \epsilon = E_1 - E_2 \):

\[
\beta = \frac{2 \gamma_l a_{R_y}}{T_{e,m} / T_e} \exp \left( \frac{-\Delta E_1}{T_e} \right).
\]

(14)

C. General case. We obtain an approximate formula applicable to the entire region of \( T_e \). To this end, we
separate in the sum (9) the term with \( k = 1 \), and replace the
remaining sum with an integral. We then obtain

\[
\frac{1}{a^*} = \frac{2 h^2 \mu_1 \mu_2}{\hbar^2} \left[ \frac{\Delta E_1}{F_1 / \Lambda_1} + \frac{3 \gamma_1 T_e}{2 \Delta \Sigma_1 \mu_0^l} \right].
\]

(14)

This expression makes it possible to draw certain conclusions with respect to the dependence of \( \alpha \) on the
plasma composition. Thus, at low \( T_e \), as already noted, \( \alpha \) is the same for all the atoms. With increasing \( T_e \),
the specific structure of the atom comes into play. Under
these conditions, \( \alpha \) depends principally on the ratio \( \Sigma_1 / \mu_0^l \), and on the magnitude of the "gap" \( \Delta \Sigma_l \).

D. Results of calculations, comparison with experiment. Figure 2 shows the results of the calculation of
\( \alpha \) for the atoms H, Ar, He, N, K, and Cs. For each of
them, the calculations were made both by the approximate
formula (14) and by formula (9). In some cases (depending on the specific structure of the atom) we
used both \((\alpha_{n_0, n_0+1})^0\) calculated with the aid of the sum
rules, and \((\alpha_{n_0, n_0+1})^0\) obtained by using directly presently
known experimental data on the transition probabilities.
In all cases, the simple formula (14) did not result in
appreciable deviations from the more accurate values.
It can be used to calculate IF and RF in plasmas of
various composition under a wide range of conditions.

The same figure shows the calculated data of Bates and co-workers \( ^{41} \) for H, obtained by numerically solv-
ing the system of balance equations of the excited atoms.
Although our calculations were performed by a differ-
ent method, on the whole the agreement is satisfactory.
It is not so good in the region \( T_e = (8-16) \times 10^3 K \). It is
important that it is precisely here that α is the most sensitive to the form of the cross section of the 1 → 2 transition at the threshold. This cross section was obtained by Bates from Gryzinski, i.e., not in the same way as we did. Figure 2 shows also the experimental data from [14], which are in fair agreement with the calculated ones.

We proceed to discuss the dependence of α on the singularities of the structure of the atom. At $T_e < 3000^\circ K$ we have $\alpha \sim T_e^{3/2}$ for all elements, as is well confirmed by numerous measurements made on H, He, and Ar atoms. The $T_e^{3/2}$ law has, naturally, greater applicability. For He, which has the maximum gap $\Delta E_0$, the deviation from $T_e^{3/2}$ begins much earlier (the case of Ar is discussed below). Hydrogen and nitrogen occupy an intermediate position.

The specific structure of the atom is manifest not only in the value of $\Delta E_0$. Formula (14) explains the practical coincidence of $\alpha$ for the pairs H, N and He, Ar. These atoms have close values of $\Sigma_{j=1}^l g_j$.  

**IONIZATION AND RECOMBINATION FUNCTIONS WITH ALLOWANCE FOR RADIATION**

When the influence of the radiation yield is significant, the calculation of $\alpha$ differs from that of $\beta$, since these quantities depend differently on the electron concentration. In the presence of reabsorption, an additional difference is due to the influence of the linear dimensions of the plasma and other parameters that determine the effective lifetimes. Allowance for all these effects is based on formulas (6). Let us discuss the extreme cases and possible simplifications.

If we decrease $n_e$ and by the same token increase the role of the radiation, then we obtain from (6) in the limit the so-called coefficient of "radiative recombination"

$$\alpha = (n_e n) \sum_k \nu_{ek}.$$  

This approximation is valid if the following inequalities hold for the levels that contribute to $\sum \nu_{ek}$:

$$\frac{n_{ek+1} K_n}{\langle \varepsilon_{en+1} + \varepsilon_{ek} \rangle} \gg 1, \quad \frac{\nu_{ek+1}}{n_e} (n_e \sum_k S_k) \gg 1.$$  

The first inequality means that the excited atom is more likely to emit than to experience an inelastic collision. The second inequality indicates that the "radiative recombination" coefficient (15) must be larger under these conditions than the "triple recombination" function calculated in the preceding section, multiplied by $n_e$.

If the inequalities (16) are reversed, the radiation yield becomes negligible, and we return to the formulas of the preceding section. In the intermediate conditions there occurs the so-called "impact-radiation" recombination. We shall discuss its qualitative features.

The intensity of the radiative processes decreases rapidly with increasing $k$, and the intensity of the impact processes increases. Therefore, the energy interval can be broken up into two regions: $E_k > E_R$, where the recombination is determined by the radiation, and $E_k < E_R$, where collision processes predominate.

Let us consider the case of low temperatures and let us estimate the influence of the radiation on $\alpha$. Obviously, this influence is significant only if the level $E_R$ lies above the lower limit $7 T_e/2$ of the bottleneck. By the same token, the length of the bottleneck decreases, as can be roughly estimated by modifying formula (11) in a natural manner:

$$\alpha^{1-2} = \frac{3 \pi e m^2}{2 \hbar c} \frac{\nu_{H}}{\nu_{H}} \frac{T_e^{11} \chi (E_n / T_e)}{X^{11}}.$$  

The value of $E_R$ can be determined from the condition $\Pi E_R = 1$. If we take into account the fact that the strongly excited states are hydrogen-like, we can obtain the following approximate expression:

$$E_R \approx \frac{\hbar c}{H} \frac{\nu_{H}}{\nu_{H}} \left( \frac{\nu_{H} e^2 \hbar}{\nu_{H} \nu_{H}} \right)^{1/2} c_1 = (3 - 4) \cdot 10^7 \sec^{-1}.$$  

Inasmuch as the function $\chi$ is continuous, it follows from (18) that at low temperatures, when $n_e$ is appreciably decreased, the radiation does not influence $\alpha$ as strongly. The situation is different at high $T_e$, when the radiation can exert a strong influence on $\alpha$, and still not shift the bottleneck from the energy interval $E_1 - E_2$. Then

$$\alpha = \frac{h \nu_{H} \xi}{\pi m^2 \Delta E T_e^{5/2}} \sum_k \nu_{ek} \exp \left( \frac{E_k}{T_e} \right) \Pi_k.$$  

With further decrease of $n_e$, it is necessary to use the general expression, since $S_k$ becomes comparable with $\sum_k S_k$.  

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43In complicated atoms with splitting in $l$, it is convenient to combine into one level groups of nearly-equal-energy states that are in relative equilibrium. For example, for nitrogen such a level, with $k = 1$, is the state of the main configuration.
The radiation has entirely different effects on $\alpha$ and $\beta$. At high temperatures it has little effect on $\beta$. Indeed, the factor $\Pi_1$ in (19) drops out completely from the expression from $\beta$ at high temperatures (when $S_1 \gg \sum_k S_k$). At low temperatures, to the contrary, the radiation has little effect on $\alpha$, but it can radically alter $\beta$. In fact, under these conditions

$$\beta = K_1(\alpha \Pi_1)^{-1}, \quad (20)$$

where $\alpha$ is given by formula (17). Figure 3 shows the dependence of $\alpha K_1/\beta$, for a mixture of argon with potassium on $R$; $R$ is the linear dimension of the plasma and $\xi$ is the ratio of the number of potassium atoms and the number of argon atoms. It follows from Fig. 3 that $\Pi_1$, can reach quite large values, particularly for small $n_0$. Naturally, the use of the detailed-balancing relation $\beta = \alpha K_1 n$ is not valid under such conditions.

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1. L. E. Gurevich, Fizicheskaya kinetika (Physical Kinetics), Gostekhizdat, 1941.