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EXCITED-STATE DISTRIBUTION OF ATOMS IN THE ABSENCE OF EQUILIBRIUM

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The nonequilibrium state distribution of atoms is obtained with the aid of the one-quantum approximation and the Fokker-Planck equation, for conditions when the kinetics of their production and annihilation are determined by collisions with electrons. The results are used to explain the experimentally observed deviations from the Boltzmann distribution.

IN a nonequilibrium stationary plasma, the concentration of the atoms at any excited level is usually determined from the balance conditions for all the elementary processes that lead to population and depletion of the given level. Solution of the corresponding system of balance equations yields the distribution of the excited atoms over the states and the concentrations of the charged and neutral particles in the plasma. The solution of the problem in this formulation is quite a complicated matter.

In this paper we consider the problem in a simpler formulation. It is assumed that the concentration of the neutral atoms (N_a), electrons (N_e), and ions (N^+) are known. The velocity distribution of the electron is Maxwellian with a specified temperature T_e, which may differ from the temperature of translational motion of the heavy particles T_a. Inasmuch as there is no equilibrium, the concentrations N_a, N_e, and N^+ are not interrelated by Saha's formula with T_e or T_a. The system is stationary, since it is assumed that there exist "sources" that maintain the specified values of N_a, N_e, N^+, T_a, and T_e. It is required to find the distribution of the excited atoms over the states.

Even in this simplified formulation, the obtained system of balance equation is quite cumbersome, and can be solved for concrete conditions only numerically.[1-3]

There is no doubt that by far not all elementary processes have the same significance for the determination of the atom concentration at a given level. Thus, over a rather wide range of plasma parameters, the collision processes with the greatest probability are transitions between neighboring energy states.[1] With increasing energy gap, the probabilities of the corresponding transitions decrease rapidly. The latter circumstance indicates that on the average the energy of the bound optical electron changes little in atomic collisions, and that these changes can be regarded as a slow probabilistic process of the Brownian motion type in energy space.[4] Assuming here that the energy in the atom changes in quasi-continuous fashion, we can reduce the problem to the solution of a Fokker-Planck differential equation. Pitaevskiĭ and Gurevich[5-7] used it successfully to describe the kinetics of recombination. However, the assumption that the energy changes quasi-continuously is hardly justified for transitions between ground and first-excited states in an atom, where the energy of the bound electron changes markedly. This limits the applicability of the Fokker-Planck equation.

In this paper we use two approaches that are close in character and supplement each other to some degree: the Fokker-Planck diffusion equation and the so-called one-quantum approximation. In the latter case we take into account the discrete nature of the levels of the atom, but consider only transitions between neighboring states. The one-quantum approximation was used earlier to determine the distribution of molecules over the vibrational states.[8] We have called attention to the possibility of using it to determine the concentrations of excited atoms. On the basis of a comparison of the results obtained with the aid of the one-quantum approximation and the Fokker-Planck equation, we propose an approximate expression for the determination of the atom concentration at any level, with account taken of the discreteness of the levels and the different transitions between them. The results are compared with numerical calculations and are used to explain the non-equilibrium state distribution of the atoms, observed in arcs.[9-10]

For simplicity we confine ourselves to plasma conditions such that the radiative processes play a

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[1] We do not consider here the possible deviation from this fact, connected with the presence of forbidden transitions, implying that we are dealing with transition probabilities averaged over sets of terms.

secondary role in the kinetics of production and annihilation of the excited states. This means, first, that the plasma must be optically dense for lines of the resonance series, so that the latter are strongly reabsorbed and the radiation yield in them is not significant. Second, the electron concentration must be large enough to make radiative transitions between excited states much less frequent than the corresponding impact transitions, and by the same token prevent them from noticeably influencing the distribution of the excited atoms.

ONE-QUANTUM APPROXIMATION

We start the solution of the problem in the so-called one-quantum approximation. According to the latter, a bound electron can execute transitions in which the principal number changes by ±1, i.e., to neighboring levels. As was already noted, such transitions are more frequent than transitions in which the principal quantum number changes by ±2, ±3, etc. Let us analyze this assumption for the case of collisions with free electrons. We write the balance equation for the atoms at the i-th level

$$\sum_{k\neq i}{}^{'} (N_k w_{ki} - N_i w_{ik}) = 0, \tag{1}$$

where w_{ki} is the probability of the transition k → i per unit time, averaged over the distribution of the free electrons. The summation in (1) is over all the discrete states realized in the plasma, and the state e corresponding to the continuum. It is convenient to introduce the relative concentrations

$$y_i = N_i / N_i^0, \tag{2}$$

where N_i^0 is the concentration of the atoms at the level i under equilibrium conditions. Using (2), we get from (1)

$$\sum_{k\neq i}{}^{'} = N_i^0 w_{ik} (y_k - y_i) = 0. \tag{3}$$

The quantity $N_i^0 w_{ik} = N_k^0 w_{ki}$ characterizes the frequency of the i → k transitions. According to our assumption

$$A_i = N_i^0 (w_{i,\,i+1} + w_{i,\,i-1}) \gg B_i = \sum_{k\neq i,\, i\pm1}{}^{'} N_i^0 w_{ik}.$$

In the Bethe-Born approximation[11]

$$N_i^0 w_{ik} = N_a N_e \frac{4\sqrt{2\pi}\, e^4 \Lambda g_i f_{ik}}{\Sigma_a(f_0)\sqrt{mkT_e}\,(E_i - E_k)} \times \exp\left[\frac{\max(E_i, E_k)}{kT_e}\right], \tag{4}$$

where

$$\Sigma_a(f_0) = \sum g_n e^{E_n/kT_e}$$

is the partition function,[2)] g_n the statistical weight of the level n, $E_n = \mathrm{Ry}/n^2$ the energy of the level n, n the effective quantum number, Ry the Rydberg constant, f_{ik} the oscillator strength of the i → k transition, and Λ the Coulomb logarithm. For the ionization probability we use the data of [12].

The table lists the ratios B_i/A_i calculated for different states of hydrogen. For bound-bound transitions we have here $\Lambda \approx 0.2$.[13] As seen from the table $B_i/A_i \ll 1$ in this temperature range. We note that although these results were obtained in the Bethe-Born approximation, the conclusions do not change qualitatively when other universally accepted approximations are used. In particular, similar estimates made in the Born approximation resulted in no appreciable differences.

i	T, 10^3 °K	
	5	12
1	0.001	0.035
4	0.07	0.10
8	0.09	0.10

We thus obtain the solution of the balance equation, confining ourselves to the most important transitions i → i ± 1. We obtain in place of (3)

$$N_i^0 w_{i-1,\,i}(y_{i-1} - y_i) - N_i^0 w_{i,\,i+1}(y_i - y_{i+1}) = 0. \tag{5}$$

Since there is no detailed balancing, impacts of the first kind do not compensate for impacts of the second kind, and a stationary solution is possible if

$$N_i^0 w_{i,\,i+1}(y_i - y_{i+1}) = \text{const}. \tag{6}$$

For the last state $\tilde{n}$ realized under the given conditions we have[14]

$$N_{\tilde{n}} w_{\tilde{n}e}(y_{\tilde{n}} - y_e^2) = \text{const}, \tag{7}$$

where y_1 and y_e^2 are known. Thus, in the case of not too high temperatures, $y_1 = N_1/N_1^0 = \Sigma_a(f_0)/\Sigma_a(f)$, where f_0 and f are the equilibrium and non-equilibrium distribution functions, and $\Sigma_a(f_0)$ and $\Sigma_a(f)$ are the corresponding partition functions of the atom.

Solving (6), we obtain

[2)] We took into account the fact that the energy of the bound state in the atom is $E_n < 0$, so that E_n is henceforth taken to mean $|E_n|$.

$$\text{const} = j = \frac{(1-y_e{}^2)N_e}{\Sigma_a(f)\Sigma_1{}^e}, \qquad y_i = \frac{\Sigma_i{}^e + y_e{}^2\Sigma_1{}^{i-1}}{\Sigma_1{}^e}, \tag{8}$$

where

$$\Sigma_i{}^j = \sum_{n=i}^{j} \frac{\exp(-E_n/kT_e)}{g_n\,w_{n,\,n+1}}$$

The physical meaning of j in (8) can be readily established from (6). We see that it is proportional to the number of bound electrons going over per unit time from the state i to the state i + 1, i.e., j is the particle-number flux. From (8) we see that under equilibrium ($y_e^2 = 1$) we have j = 0. If $y_e^2 > 1$, the flux is directed toward negative energies and the processes of recombination and quenching prevail over excitation and ionization. The opposite obtains if $y_e^2 < 1$. When i = 1 we have $y_1 = 1$, and $y_i \to y_e^2$ for sufficiently large i.

We represent $w_{i,\,i+1}$ in the form

$$w_{i,\,i+1} = N_e \exp\left(-\frac{E_i - E_{i+1}}{kT_e}\right)\bar{v}\,\bar{\sigma}_{i,\,i+1}, \tag{9a}$$

where $\bar{v}$ is the average velocity of the free electrons, and $\bar{\sigma}_{i,\,i+1}$ is the averaged excitation cross section. Then

$$j = \frac{1-y_e{}^2}{\Sigma_a(f)\,\Omega_1{}^e/\bar{v}}, \qquad y_i = \frac{\Omega_i{}^e + y_e{}^2\Omega_1{}^{i-1}}{\Omega_1{}^e}, \tag{9}$$

where

$$\Omega_i{}^j = \sum_{n=i}^{j} \frac{\exp(-E_{n+1}/kT_e)}{g_n\bar{\sigma}_{n,\,n+1}}.$$

By the same token we know the particle concentration at any level.

A shortcoming of the one-quantum approximation is that no account is taken of the transitions i → i ± k with k ≥ 2. We consider another method of solution, in which these transitions are taken approximately into account.

THE FOKKER-PLANCK EQUATION

Following [4-7], we regard the change in the energy of a bound optical electron in an atom as a diffusion process, assuming that the energy changes quasi-continuously. The corresponding expression for the flux, obtained from the Fokker-Planck equation, has under stationary conditions the form[5]

$$j = B(E)g(E)(\partial f/\partial E - f/kT_e), \tag{10}$$

$$B(E) = {}^1\!/_2\,\partial\overline{(\Delta E^2)}/\partial t. \tag{11}$$

is the diffusion coefficient, proportional to the rms change in the energy of the bound state per unit time. The density g(E) of the number of states can be related with the statistical weight of an individual state by means of

$$g(E_n) = g_n n^2(n+1)^2/(2n+1)\,\mathrm{Ry}. \tag{12}$$

Substituting in (10) $f = [\Sigma_a(f)]^{-1}y(E) \times \exp(E/kT_e)$, we obtain its solution under the boundary conditions $y(E_1) = 1$ and $y(0) = y_e^2$:

$$j = \frac{1-y_e{}^2}{\Sigma_a(f)I_0{}^{E_1}}, \qquad y(E) = \frac{I_0{}^E + y_e{}^2 I_E{}^{E_1}}{I_0{}^{E_1}}, \tag{13}$$

where

$$I_a{}^b = \int_a^b \frac{\exp(-E/kT_e)}{B(E)g(E)}\,dE.$$

The validity of the obtained expressions for the lower excited states is doubtful, since the jump-like change in energy during the transitions is very significant here. At the same time, the structure of (13) is very similar to that of formulas (8) of the one-quantum approximation, where the discreteness is taken into account correctly. Using this analogy, let us attempt to modify (13) somewhat in a way as to take into account the discreteness of the atomic levels. To this end we substitute in (13) g(E) as given by (12), make the substitution

$$dE \to \Delta E \to E_n - E_{n+1} = (2n+1)\,\mathrm{Ry}/n^2(n+1)^2$$

and go over from integration with respect to E to summation with respect to n. We obtain

$$j = \frac{1-y_e{}^2}{\Sigma_a(f)\overline{\Sigma}_1{}^e}, \qquad y_i = \frac{\overline{\Sigma}_i{}^e + y_e{}^2\overline{\Sigma}_1{}^{i-1}}{\overline{\Sigma}_1{}^e}, \tag{14}$$

where

$$\overline{\Sigma}_i{}^j = \sum_{n=i} \frac{\exp(-E/kT_e)}{g_n\bar{w}_n}; \quad \bar{w}_n = \frac{B(E_n)}{(E_n - E_{n+1})^2}. \tag{15}$$

We see that (14) differs from (8) only in that $\bar{w}_n$ is replaced by $w_{n,\,n+1}$. This is connected with the fact that in (14), derived on the basis of the Fokker-Planck equation, we took approximate account of the transitions i → i ± k (k ≥ 2), which are completely excluded in the one-quantum approximation. Naturally, if we go over in (14) to a quasi-continuous energy variation then, as follows from the derivation of (14), it goes over into the solution of the Fokker-Planck equation (13).

If the energy of the bound electron changes upon collision with the free electrons, the quantity $\bar{w}_n$ connected with the diffusion coefficient can be calculated. This greatly facilitates the calculations. We represent $B_n(E_n)$ in the form

$$B_e(E_n) = \frac{1}{2}\sum_k (E_n - E_k)^2 w_{nk} = \frac{1}{2}\overline{\sum_k{}' (E_n - E_k)^2\sigma_{nk}v}, \tag{16}$$

σ_{nk} is the cross section of the transition n → k, and the bar denotes averaging over the distribution of the free electrons. Let us use for σ_{nk} the Bethe-Born approximation:[11]

$$B_e(E_n) = 4\pi N_e \int {\sum_k}' (E_n - E_k)^2 |(x)_{nk}|^2 \left(\frac{e^2}{\hbar v}\right)^2 \frac{dq}{q}, \quad (17)$$

where v is the velocity of the free electron, q the momentum transfer, and $(x)_{nk}$ the matrix element of the dipole-moment projection. In the one-electron approximation the sum over k is calculated in general form:

$$\sum_k (E_n - E_k)^2 |(x)_{nk}|^2 = \frac{2m}{3} E_n. \quad (18)$$

We then obtain for the ground state

$$B_e(E_1) = \frac{8\sqrt{2\pi}\,\Lambda e^4 N_e E_1}{3\sqrt{mkT_e}} \exp\left(-\frac{E_1 - E_2}{kT_e}\right). \quad (19)$$

In the integration with respect to v we took account of the fact that the transitions from the ground state can be made by electrons whose energy is not lower than $E_1 - E_2$. Let us extrapolate (19) to arbitrary E_n, i.e., let us assume that

$$B_e(E_n) \approx \frac{8\sqrt{2\pi}\,\Lambda e^4 N_e E_n}{3\sqrt{mkT_e}} \exp\left(-\frac{E_n - E_{n+1}}{kT_e}\right). \quad (20)$$

Such an extrapolation is possible, for Eq. (20) goes over into (19) when $E_n \to E_1$. On the other hand, for small E_n the exponential factor is insignificant and (2) coincides with the value of B_e obtained in [7], where the collision of the free and bound electrons was considered quasi-classically. Using (20), we find that

$$\bar{w}_n = \frac{4\sqrt{2\pi}\,\Lambda e^4 N_e E_n}{3\sqrt{mkT_e}(E_n - E_{n+1})^2} \exp\left(-\frac{E_n - E_{n+1}}{kT_e}\right)$$
$$= \bar{v}\bar{\sigma}_n \exp\left(-\frac{E_n - E_{n+1}}{kT_e}\right) \quad (21)$$

and from (14) we get

$$y_i = \frac{\overline{\Omega}_i{}^e + y_e{}^2 \overline{\Omega}_1{}^{i-1}}{\overline{\Omega}_1{}^e} = r_1(i) + y_e{}^2 r_e(i), \quad (22)$$

where

$$\overline{\Omega}_i{}^j = \sum_{n=i}^{j} \frac{\exp(-E_{n+1}/kT_e)}{g_n \bar{\sigma}_n}. \quad (22')$$

We see that (22) goes over into (9) if $\bar{\sigma}_n$ is replaced by $\bar{\sigma}_{n,n+1}$.

Calculation of the relative concentrations by means of (22) is quite simple. We note that for a multicomponent plasma it is necessary to take $y_e y_{N^+}$, in place of y_e^2, where N^+ is the concentration of the ions of the given species.

From the form of (22) we can deduce that the y_e^2 for different atoms should not differ much under similar conditions, since the individual properties of the atoms become smoothed out to a considerable degree when sums over a large number of states are calculated.

At sufficiently low temperatures, we can simplify formula (22). Indeed, in this case the function under the summation sign in (22′) has a maximum when n ≫ 1, and the contribution of terms with small n to the sums in (22) is exponentially small. Therefore for small n the second term in the numerator of (22) plays no role and $y_i \approx 1$. Taking this into account, we can replace the summation in (22) by integration without excessive error, i.e., as indicated above, we can go over from (22) to (13). Putting $g_n = 2n^2$ and using (20), we obtain from (13)

$$y_i = \varphi\left(\frac{E_i}{kT_e}\right) + y_e{}^2\left[1 - \varphi\left(\frac{E_i}{kT_e}\right)\right], \quad (23)$$

where

$$\varphi(x) = \Phi(\sqrt{x}) - \frac{2e^{-x}\sqrt{x}}{\sqrt{\pi}}\left(\frac{2}{3}x + 1\right),$$

$$\Phi(\sqrt{x}) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2}\,dt.$$

If we leave out the first term of (23), i.e., we disregard the excitation processes, we arrive at the result obtained by Gurevich[7] for electron-ion recombination.

The results can be used also to calculate the recombination and ionization coefficients.

DISCUSSION OF RESULTS; COMPARISON WITH EXPERIMENT

Our results are based on a number of assumptions. Let us compare them with the published numerical solutions of the system of balance equations.[1-3] Thus, results of computer calculations for a hydrogen plasma were represented in [1] in the form

$$y_i = r_1'(i) + y_e^2 r_e'(i).$$

The coefficients r_1' and r_e' were tabulated. We compared them[3] with the coefficients r_1 and r_e introduced by us in (22) and obtained perfectly satisfactory agreement. The discrepancies did not go beyond the limits of the accuracy with which the

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[3] The coefficients r'_1 and r'_e depend on N_e, since relative processes were taken into account in their calculation in [1]. We compared them for sufficiently large N_e, when the radiative processes play no role.

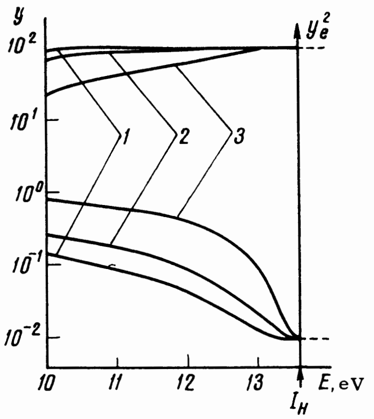

FIG. 1. Plot of y vs. E for hydrogen (formula (22)). Curves 1, 2, and 3 correspond to temperatures T_e = 12000, 8700, and 5000°K. (The energy is reckoned from the ground state.)

effective cross sections used in the calculations of [1] are known. This confirms the correctness of our assumptions.

Let us turn to Eq. (22) for y. For fixed y_e^2 the value of y depends on the temperature T_e. Figure 1 shows a plot of y against E for hydrogen at different T_e and for two values of y_e^2, 10^{-2} and 10^2.

We see that for recombination ($y_e^2 = 10^2 \gg 1$) most excited states are in relative equilibrium with the continuous spectrum $y_i \approx y_e^2$,[14] and that the number of such states increases with increasing temperature. This phenomenon was observed experimentally in recombination decay of a helium plasma.[15]

The situation is different if ionization predominates, $y_e^2 \ll 1$. The distribution of the atoms over the states differs strongly from equilibrium. Only the strongly excited states are in equilibrium with the continuous spectrum. At low temperatures a tendency is observed to establishment of a relative equilibrium between the ground and first-excited state $y_i \approx 1$. We see that for many states ($i = 3-7$) we have approximately $\ln y \sim E$, so that we can speak of a quasi-Boltzmann distribution with a temperature lower than that of the electrons.

Such nonequilibrium distributions of the atoms over the excited states were observed experimentally in arcs at atmospheric pressure.[9, 10] The most complete measurements, which permit a comparison of the results with the experimental data, were made by Kolesnikov.[9] He calculated the excited-state distribution of the atoms in an arc-discharge plasma in an argon atmosphere ($N_{Ar} = 2 \times 10^{18}$ cm^{-3}) to which hydrogen was added ($N_H = 1.6 \times 10^{17}$ cm^{-3}). The local values of the concentrations of the atoms and electrons are given in [9] for a current i = 4A ($N_e = 2 \times 10^{15}$ cm^{-1} on the axis). Unfortunately, Kolesnikov measured at this current only the electron temperature averaged over the arc column (T_e = 8700 ± 200° K). However, knowing this average value, the character of the averaging made during the measurement, and the relative variation of the electron temperature in the radial direction (from measurements at other currents made in [9]), we can obtain the local values. The electron temperature on the arc axis was approximately 9300° K. We shall henceforth speak exclusively of local values of the measured quantities, taken on the axis of the arc.

Kolesnikov[9] established that the investigated plasma is not in equilibrium, and that the excited-state distribution of the atoms is quasi-Boltzmann with a temperature much lower than that of the electron, and quite close to that of the atoms (T_a = 3300° K). On this basis he proposed that the excited-state distribution of the atoms is determined by elastic collisions with the atoms.

It seems to us that in this case the atomic collisions are not the cause of such a distribution. In fact, a similar situation can arise also if the concentration of the charged particle is much lower than the values calculated from the Saha formula with T_e. Using the data on the equilibrium composition of the investigated plasma given in [9] we find that actually, on the axis, $y_e y_{Ar^+} \approx y_e y_{H^+} \approx 1.3 \times 10^{-2}$ (y_{Ar^+} and y_{H^+} are the relative concentrations of the ions Ar and H). An investigation of the causes of the latter circumstance is already beyond the scope of this paper, since we are interested only in the distribution of the atoms over the excited states. We note, however, that this can be brought about by diffusion of the electrons from the central hot parts of the arc channel to the cold peripheral regions, where they recombine. The neutral particles become ionized there when they penetrate from the peripheral regions into the central ones.

Estimates show that under the conditions in question the kinetics of production and annihilation of the excited states are determined by collisions with the electrons. The radiative processes are not essential for the reasons indicated above. Collisions with atoms, for transitions between the ground and excited states, are not effective compared with the electrons. As regards the efficacy of these collisions for transitions between excited states, indirect data can be obtained here by comparing the diffusion coefficients $B_e(E)$ and $B_a(E)$ (formula (A.1) of the Appendix). The atomic collisions could compete here with the electronic ones only if the cross sections were exceedingly high, $\sigma \gtrsim 10^{-13}$ cm^2 (here σ is the transport cross section for the scattering of a slow electron by an atom). Thus, under these conditions the atomic collisions are apparently insignificant for all values of the bound-state energy.

Consequently, we shall use (22) to determine the concentrations of the excited atoms. The values of y for hydrogen, calculated from (22), are shown in Fig. 2, which shows also the points corresponding to experimentally measured hydrogen concentrations at the levels with i = 3, 4, 5, and 6. We see that theory and experiment agree satisfactorily. A variation of ± 200° K in the electron temperature on the axis led to no significant differences.

We note that in a recent paper by Keck and Carrier[16] devoted to related problems, but as applied principally to molecules, nonequilibrium distributions of the particles over the vibrational states were obtained for different model potentials, using either the one-quantum approximation or the Fokker-Planck equation. In particular, the distribution obtained with the aid of the Fokker-Planck equation for a classical Coulomb oscillator, is used by the authors for the determination of the concentration of the excited atoms. In spite of the fact that such a model is rather crude, surprising agreement with experiment was obtained.[15] We have noted that under the conditions given in [15] the concentration of the atoms at the upper excited levels were in equilibrium with the electrons, and therefore the agreement of the results still does not confirm the theory. For the lower excited states, whose populations are essentially not in equilibrium, there can be no agreement in principle, since the radiative processes can by no means be neglected for them. On the other hand, they are not considered in the theoretical paper.[16]

In conclusion, the author is sincerely grateful to L. M. Biberman and I. T. Yakubov for discussions and help with the work.

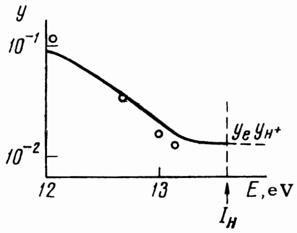

FIG. 2. Comparison of the experimental and calculated values of y on the arc axis. The points correspond to the H concentrations measured in [14]. The solid curve was calculated from (23), T_e = 9300°K, $y_e y_{H^+} = 1.3 \times 10^{-3}$. The arrow indicates the ionization potential. (The energy is reckoned from the ground state.)

APPENDIX

COLLISIONS WITH ATOMS

Conditions are possible, under which the energy of the bound state is changed by collisions with atoms (in the ground state). The diffusion coefficient $B_a(E)$ for weakly-bound states was calculated by Pitaevskiĭ:[15]

$$B_a(E) = 128\sqrt{2}(kT_a)\sqrt{m}\sigma N_a E^{3/2} / 3\pi M, \qquad (A.1)$$

where σ is the transport cross section for the scattering of an electron by an atom and M is the mass of the atom. (A.1) is valid if $kT_a \ll \sqrt{m/Me^2}/a$ (a is the dimension of the atom). For this case we can use expressions (8) and (14), in which we make the substitutions $T_e \rightarrow T_a$, $B \rightarrow B_a$, and $\bar{w}_k \rightarrow \bar{w}_k^a$ (the index a denotes that these quantities characterize an atomic collision). In particular, at low temperature we obtain in place of (23)

$$y_i = Z\left(\frac{E_i}{kT_a}\right) + y_e^2\left[1 - Z\left(\frac{E_i}{kT_a}\right)\right], \qquad (A.2)$$

where $Z(x) = 1 - e^{-x}(1 + x)$. It is necessary to satisfy here the condition $E_n/kT_a \sim 1$ for $n \gg 1$.

However, more interesting conditions are those when the collisions with electrons and atoms must be taken into account simultaneously. In this case it is important to find the distribution function F_0 at which j = 0. It will not be an equilibrium function, because $T_a \neq T_e$. Physically, the equation j = 0 denotes that a chemical equilibrium was established in the nonequilibrium system, i.e., the total number of ionization acts is equal to the number of recombination acts. F_0 plays the role so to speak of a "quasi-equilibrium" distribution function in the presence of two temperatures. Let us find F_0 in the one-quantum approximation. We write the flux in the presence of collisions with the electrons and the atoms:

$$j/N_a = N_i(w_{i,\,i+1}^{a} + w_{i,\,i+1}^{c}) - N_{i+1}(w_{i+1,\,i}^{e} + w_{i+1,\,i}^{a}). \qquad (A.3)$$

Solving (A.3) for j = 0 we obtain

$$\frac{N_i}{N_1} = \frac{g_i F_0(E_i)}{g_1 F_0(E_1)} = \prod_{n=1}^{i-1} P_n, \qquad (A.4)$$

where

$$P_n = g_{n+1}\left[N_e \exp\left(-\frac{E_n - E_{n+1}}{kT_e}\right)\bar{v}_e\bar{\sigma}_{n,\,n+1}^{e} + N_a \exp\left(-\frac{E_n - E_{n+1}}{kT_a}\right)\bar{v}_a\bar{\sigma}_{n,\,n+1}^{a}\right]$$
$$[g_n(N_e\bar{v}_e\bar{\sigma}_{n,n+1}^{e} + N_a\bar{v}_a\bar{\sigma}_{n,n\div1}^{a})]^{-1}. \qquad (A.5)$$

In the derivation of (A.6) we used (9a). From (A.5) and (A.4) we see that when $T_e = T_a$ (A.4) goes over into the usual Boltzmann formula. We can find directly from (A.5) the conditions under which atomic collisions can be neglected.

It can be shown that if we make in (A.5) the substitution $\sigma_{n,n+1} \to \bar{\sigma}_n$ and then go over to quasi-continuous variation of the energy, then the F_0 obtained in this manner will coincide with the F_0 derived directly from the Fokker-Planck equation in which account is taken of collisions with two types of particle.

Knowing F_0, we can solve the "non-equilibrium" problem, when $j \neq 0$. It is convenient to introduce the relative concentrations, which are now referred to the distribution function F_0:

$$J(E_i) = N_i / N_i(F_0), \tag{A.6}$$

where $N_i(F_0)$ is the concentration of the atoms at the level i, calculated with the distribution function F_0; formally j and $J(E_i)$ are obtained from (14) by making the substitutions

$$e^{E_n/kT_e} \to F_0(E_n), \quad \bar{w}_n \to \bar{w}_n^e + \bar{w}_n^a = \frac{B_e(E_n) + B_a(E_n)}{(E_n - E_{n+1})^2}.$$

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