

## ASYMPTOTIC THEORY OF THE UNBALANCED IONIZATION LAYER NEAR A CATALYTIC WALL IN PLASMA OF MOLECULAR GASES\*

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The statement and asymptotic solution of the problem of deviation from ionization equilibrium in a moderately ionized gas near a perfect catalytic wall was previously considered in /1/ in the case when atoms are ionized by an electric shock and in the ion-electron recombination an electron participates as the third body. A different case of chemical kinetics is considered here in which atom ionization by collision with neutral molecules and the ion-electron recombination with neutral molecules as the third body play an important part besides reactions and recombinations of the indicated type.

1. Statement of the problem. Let us consider a moderately ionized multicomponent gas consisting of  $M$  neutral components, positive single-charge ions of atoms of one of the neutral components (easily ionizable additives), and electrons. The additive atoms are ionized by collision with electrons, as well as with molecules of one of the neutral components (below called component I); electrons or molecules of the first component may participate in the ion-electron recombinations as the third body. For simplicity of exposition we assume that the gas as a whole is at rest and its pressure constant; that in the considered temperature range the dependence of all binary diffusion coefficients  $D_{jk}$ , where subscript  $j$  relates to ions or electrons and  $k$  to any of the neutral components of the mixture, is the same. The distribution of charges and variation of molar concentration of neutral components throughout the gas volume is assumed negligible, and the gas temperature is assumed to be a known monotonically increasing function of the  $y$ -coordinate (the  $y$ -axis is directed along the normal to the wall).

On the above assumptions the distribution of the quasineutral molar concentration of charged particles  $x$ , in the presence of electric current as well as in its absence, is defined by the equation of ambipolar diffusion /2/. For the considered here model that equation and boundary conditions are of the form

$$(d/dy)(nDdx/dy) = n^2(k_{re}x + k_{r1}x_1)(x^2 - x_r^2), \quad y = 0, \quad x = 0; \quad y \rightarrow \infty, \quad x \rightarrow x_{r\infty}$$

$$D = 2D_i D_e (D_i + D_e)^{-1}, \quad D_j^{-1} = \sum_{k=1}^M x_k D_{jk}^{-1} \quad (j = i, e), \quad x_r = n_e n^{-1}$$

where  $n$  is the over-all numerical concentration of particles in the mixture,  $k_{re}$  and  $k_{r1}$  are components of the recombination rate for reactions in which the part of the third body is played by electrons and first component molecules, respectively,  $x_k$  is the molar concentration of the  $k$ -th neutral component, and  $n_e$  is the local chemically stable concentration of charged particles. The subscript  $\infty$  denotes here and subsequently the quantities in the unperturbed region away from the wall.

We convert the problem to dimensionless variables  $\eta = y/L, z = x/x_{r\infty}$ , where  $L$  is a characteristic scale of temperature variation. We have

$$\chi (a z')' = b(1 + cz)(z^2 - r^2), \quad \eta = 0, \quad z = 0; \quad \eta \rightarrow \infty, \quad z \rightarrow 1 \quad (1.1)$$

$$\chi = \frac{d_{1\infty}^2}{2L^2}, \quad d_1 = \left( \frac{2D}{k_{r1} n_1 n_e r} \right)^{1/2}, \quad a = a(\eta) = \frac{nD}{n_{\infty} D_{\infty}}$$

$$b = b(\eta) = \frac{k_{r1} n^3}{k_{r1\infty} n_{\infty}^3}, \quad c = c(\eta) = \frac{k_{re} n_e r_{\infty}}{k_{r1} n_1 n_{\infty}}, \quad r = \frac{x_r}{x_{r\infty}} = \theta^{1/2} e^{-t}$$

$$\theta = \theta(\eta) = T/T_{\infty}, \quad t = m\eta, \quad m = I/(2kT_{\infty}), \quad q = (1 - \theta)/\theta$$

where  $n_1$  is the concentration of first component molecules,  $T$  is the temperature of gas,  $I$  is the potential of ionization of the additive atoms,  $k$  is the Boltzmann constant, and the prime denotes differentiation with respect to  $\eta$ . The quantity  $d_1$  has the meaning of the local recombination length for recombination reactions with participation of the first component molecules. We also introduce the over-all recombination length by formula

\*Prikl. Matem. Mekhan., 44, No. 5, 839-846, 1980

$$d = \left[ \frac{2D}{(k_{re} n_{er} + k_{r1} n_1) n_{er}} \right]^{1/2}$$

The function  $c(\eta)$  defines the ratio of reaction rate with electron participation to that with a neutral molecule.

In the case of plasma of combustion products with alkaline additive at  $T_\infty = 2700$  K, 1 atm pressure, 1% molar concentration of the additive (potassium), 18% molar concentration of the first component (water molecules), and taking the expressions for  $k_{re}$  and  $k_{r1}$  from the paper by A. Kh. Mnatsakanian and G. V. Haidus, Ionization of atoms and recombination of atomic ions and electrons in unsteady atomic-molecular plasma. Preprint No. 1-43 of the Inst. of High Temperatures, Akad. Nauk, SSSR, Moscow, 1979, we obtain  $c_\infty = 0.7$ . Note that according to that publication it is generally possible to assume in this case the temperature function  $c$  as being approximately constant.

In the particular case of constant temperature of gas  $a \equiv b \equiv r \equiv 1$ , and  $c \equiv \text{const}$  problem (1.1) has the exact solution

$$z = \tau \{ \eta [(c+1)/(2\chi)]^{1/2}, c \}$$

$$\tau(u, v) = (v^2 - 6v - 10v - 3v + 1)(v^2 + 6v + 2v - 3v + 1)^{-1}$$

$$v = \{ [3(v+1)(3v+8)]^{1/2} + 5 + 3v \} e^{2u}$$

For the molar concentration of charged particles and the molar concentration derivative at the wall (the quantity that determines the limit flux of particles to the wall), represented in initial variables, we obtain

$$x = x_r \tau \left( \frac{y}{d}, c \right), \quad \left( \frac{dx}{dy} \right)_w = \left( \frac{3c+8}{3c+3} \right)^{1/2} \frac{x_r}{d} \quad (1.2)$$

where, and subsequently, the subscript  $w$  indicates quantities at the wall.

The dependence of  $\tau$  on  $u$  in the case of  $v=0$  and  $v=2$  is shown in Fig.1, where the dash line is the curve of function  $\text{th } u$  which is the limit form of function  $\tau(u, v)$  at high values of parameter  $v$ .

For the derivation of the approximate analytic solution of problem (1.1) in the general case of variable gas temperature we use the asymptotic method proposed in [1/].

2. The hot wall limit ( $\chi \rightarrow 0$ ). The external asymptotic expansion of the solution of problem (1.1) is of the form

$$z(\eta; \chi) = r(\eta) + \dots$$

and the internal expansion of the form

$$z(\eta; \chi) = z_1(\eta_1) + \dots; \quad \eta_1 = \eta / \sqrt{\chi}$$

For function  $z_1$  we have the boundary value problem

$$a_w d^2 z_1 / d\eta_1^2 = b_w (1 + c_w z_1) (z_1^2 - r_w^2), \quad \eta_1 = 0, \quad z_1 = 0; \quad \eta_1 \rightarrow \infty, \quad z_1 \rightarrow r_w$$

whose solution in input variables yields

$$x = x_{rw} \tau \left( \frac{y}{d_w}, c_w r_w \right), \quad \left( \frac{dx}{dy} \right)_w = \left( \frac{3c_w r_w + 8}{3c_w r_w + 3} \right)^{1/2} \frac{x_{rw}}{d_w} \quad (2.1)$$

for the molar concentration of charged particles in an unsteady layer and for the molar concentration derivative at the wall.

3. The cold wall limit ( $\chi \rightarrow 0, m^{-1} \rightarrow 0$ ). We introduce the parameter of comparison  $\gamma = \gamma(\chi)$  which is the root of equation  $\gamma = \chi \ln^2 \gamma$ . It can be shown that

$$\gamma = \chi \ln^2 \chi [1 + O(\ln \ln \chi^{-1} / \ln \chi^{-1})]$$

We establish between the small parameters  $\chi$  and  $m^{-1}$  the following relation of order:  $m / \ln \gamma^{-1} \rightarrow k_1$ , where  $k_1$  is a specified positive constant.

The external expansion of problem (1.1) is associated with the limit  $\chi \rightarrow 0, m^{-1} \rightarrow 0$  and fixed  $\eta$ . It is of the form

$$z(\eta; \chi, m) = r [1 + a(2\theta^{1/2} b)^{-1} (k_1 q')^2 \exp(mq - \ln \gamma^{-1}) + \dots] \quad (3.1)$$

Note that in the indicated passing to limit, function  $r = r(\eta; m)$  tends to vanish, hence in calculating the second term of expansion (3.1) ionization by electron impact and the recombination with the electron as the third body was neglected since it is low in comparison with ionization resulting from collisions with neutral molecules and recombination with the molecules as the third body. In the external part of the perturbed region, where  $r = O(1)$ , it is, evidently, not possible to neglect ionization by electron impact, and expansion (3.1) is generally valid only in the first approximation. The expansion valid in the external part of the perturbed region in subsequent approximations is associated with the limit

$\chi \rightarrow 0, m^{-1} \rightarrow 0$  and fixed  $\eta_2 = m q(\eta)$ .

From the physical point of view the latter expansion is valid in the region where the gas temperature is still little different from that in the unperturbed zone, and the local chemically stable concentration of charged particles is of the same order of magnitude as the unperturbed concentration. In that region ionization and recombination reactions of both types take place. Expansion (3.1) in the inner part of the chemically stable region where  $r \ll 1$  and the reactions with electron participation are of minor importance, as compared to reactions with the participation of molecules.

The form of solution of the problem in the unsteady layer region substantially depends on the quantity  $k_1 q_w$ . Let us consider three cases.

3.1.  $k_1 q_w < 1$ . The expansion for the unsteady layer is of the form

$$z(\eta; \chi, m) = \exp(-mq_w) z_3(\eta_3) + \dots; \quad \eta_3 = \eta \ln \gamma^{-1} \exp[(\ln \gamma^{-1} - mq_w) / 2]$$

and for function  $z_3$  we have the problem

$$a_w d^2 z_3 / d\eta_3^2 = b_w (z_3^2 - \theta_w^{-1/2}), \quad \eta_3 = 0, z_3 = 0; \quad \eta_3 \rightarrow \infty, z_3 \rightarrow \theta_w^{-1/2}$$

Using the solution of this problem we obtain in initial variables

$$x = x_{rw} \tau \left( \frac{y}{d_{1w}}, 0 \right), \quad \left( \frac{dx}{dy} \right)_w = \frac{2\sqrt{6}}{3} \frac{x_{rw}}{d_{1w}} \quad (3.2)$$

3.2.  $k_1 q_w = 1$ . We introduce the parameter  $f(\chi, m) = \ln \gamma^{-1} - mq_w$  and consider three cases.

3.2.1.  $f \rightarrow \infty$ . This case is similar to that of  $k_1 q_w < 1$ , and all formulas derived in Case 3.1 apply here.

3.2.2.  $f \rightarrow k_2$ . ( $k_2$  is some specified constant). Expansion for the unsteady layer is of the form

$$z(\eta; \chi, m) = \exp(-mq_w) z_4(\eta_4) + \dots; \quad \eta_4 = \eta \ln \gamma^{-1}$$

and for function  $z_4$  we obtain the equation

$$\exp(-k_2) a_w d^2 z_4 / d\eta_4^2 = b_w [z_4^2 - \theta_w^{-1/2} \exp(-2k_1 q_w \eta_4)]$$

We introduce the auxiliary function  $\alpha$  proportional to the ratio of local recombination length for the recombination reaction with molecule participation to the characteristic scale of variation of function  $t$

$$\alpha = \frac{d_1}{\sqrt{2}} \left( -\frac{dt}{dy} \right) = -t' \left( \frac{a\chi}{br} \right)^{1/2}$$

and the new variables

$$\eta_5 = -k_1 q_w \eta_4 - 2 \ln \alpha_w, \quad z_5 = z_4 \alpha_w^{-2} \theta_w^{-1/2}, \quad \alpha_w = -k_1 q_w \left[ \frac{a_w \exp(-k_2)}{b_w \theta_w^{3/2}} \right]^{1/2} = O(1)$$

For function  $z_5(\eta_5)$  we obtain the problem

$$d^2 z_5 / d\eta_5^2 = z_5^2 - \exp(2\eta_5) \quad (3.3)$$

$$\eta_5 = -2 \ln \alpha_w, \quad z_5 = 0; \quad \eta_5 \rightarrow \infty, \quad z_5 \sim \exp \eta_5 + 1/2 + \dots \quad (3.4)$$

The curve of function  $z_5(\eta_5)$  obtained by numerical solution of the nonlinear boundary value problem (3.3), (3.4) is shown in Fig.2 for several values of parameter  $\alpha_w$  ( $\ln \alpha_w = 5; 3; 1; -1$ ), where the dash line represents the asymptotics of function  $z_5$  determined by the second of expressions (3.4) as  $\eta_5 \rightarrow \infty$ .

For the molar concentration of charged particles in the unsteady layer and for the molar concentration derivative at the wall we have in initial variables

$$x = x_{rw} \alpha_w^2 z_5 [(-dt/dy)_w y - 2 \ln \alpha_w], \quad (dx/dy)_w = \sqrt{2} \alpha_w^3 \psi_1 x_{rw} / d_{1w}; \quad \psi_1 = (dz_5 / d\eta_5)_w \quad (3.5)$$

The curve of function  $\psi_1 = \psi_1(\alpha_w)$  is shown in Fig.2, where the dash lines relate to functions determined by the asymptotic expressions at high and low values of parameter  $\alpha_w$  which are of the form

$$\alpha_w \rightarrow 0, \quad \psi_1 = 2 / (\sqrt{3} \alpha_w^3); \quad \alpha_w \rightarrow \infty, \quad \psi_1 = R \ln^{-3} \alpha_w, \quad R = [(\sqrt{6}/2) \text{ and } (0; 0, -6)]^3 = 4.134$$

where  $(s; g_2, g_3)$  is an elliptic integral of the first kind in the standard Weierstrass form  $/3/$ .

3.2.3.  $f \rightarrow -\infty$ . In this case the chemically unstable layer region is inhomogeneous, consisting of a transition and a recombination layers, each with its own asymptotic expansion.

Expansion for the transition layer is of the form

$$z(\eta; \chi, m) = \gamma z_6(\eta_6) + \dots; \quad \eta_6 = (\eta - \delta) \ln \gamma^{-1}$$

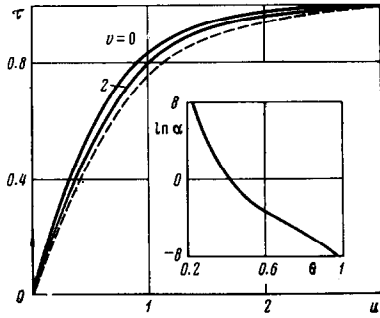


Fig. 1

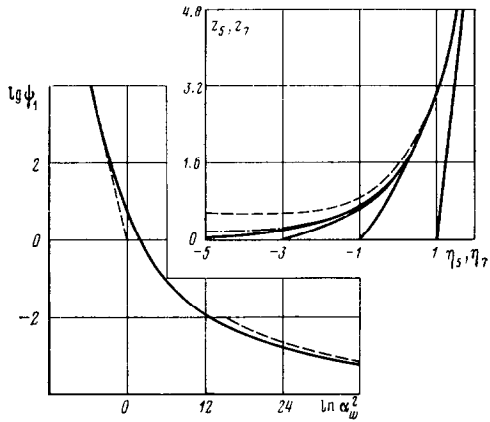


Fig. 2

where  $\delta$  is the root of the algebraic equation  $\alpha(\delta) = 1$ . It can be shown that  $\delta = O(j/m) = o(1)$ . After the substitution of variables

$$\eta_6 = \eta_7 / (-k_1 q_w'), \quad z_6 = z_7 a_w (k_1 q_w')^2 / b_w$$

Eq. (1.1) assumes the canonical form (3.3), where subscript 7 is substituted for 5. As  $\eta_7 \rightarrow \infty$  the boundary condition for this equation coincides with the boundary condition (3.4); the second boundary condition is that of damping of function  $z_7$  as  $\eta_7 \rightarrow -\infty$

$$\eta_7 \rightarrow -\infty, \quad z_7 \rightarrow 0; \quad \eta_7 \rightarrow \infty, \quad z_7 \sim \exp \eta_7 + 1/2 + \dots$$

The dash-dot line in Fig. 2 represents the curve of function  $z_7(\eta_7)$  calculated by the exact numerical solution of the considered problem.

For the subsequent merging it is necessary to know the asymptotics of function  $z_7$  as  $\eta_7 \rightarrow -\infty$ . It can be shown that it is of the form

$$z_7 \sim 6 / \eta_7^2 + \dots$$

For the molar concentration of charged particles in the transition layer we have in initial variables

$$x = x_{r\delta} z_7 [\sqrt{2} (y - y_0) / d_{1\delta}] \tag{3.6}$$

where subscript  $\delta$  denotes quantities for  $\eta = \delta$ .

The expansion for the recombination layer is related to the limit  $\chi \rightarrow 0$ ,  $m^{-1} \rightarrow 0$  and fixed  $\eta_8 = \eta / \delta < 1$ . It is of the form

$$z(\eta; \chi, m) = \chi \delta^{-2} z_8(\eta_8) + \dots$$

For function  $z_8$  we obtain the boundary value problem

$$a_w d^2 z_8 / d\eta_8^2 = b_w z_8^2, \quad \eta_8 = 0, \quad z_8 = 0; \quad \eta_8 \rightarrow 1, \quad z_8 \sim 6 a_w b_w^{-1} (1 - \eta_8)^{-2} + \dots \tag{3.7}$$

Using the solution of this problem in initial variables we find that  $(p\theta(u; g_2, g_3))$  is an elliptic Weierstrass function /3/

$$x = x_{r\delta} \frac{d_{1\delta}^2}{y_{\delta}^2} 2pe \left[ \frac{2}{\sqrt{6}} \frac{y_{\delta} - y}{y_{\delta}}; 0, -6R^2 \right], \quad \left( \frac{dx}{dy} \right)_w = 4R \frac{d_{1\delta}^2}{y_{\delta}^2} \frac{x_{r\delta}}{\delta} \tag{3.8}$$

3.3.  $k_1 q_w > 1$ . This limit case is qualitatively similar to the previous one, except that in this case the recombination layer is no longer asymptotically thin.

The direct expansion (3.1) is valid in this case for  $\eta > \eta_s$ , where  $\eta_s$  denotes the root of the algebraic equation  $k_1 q(\eta_s) = 1$ . It is important to note that parameter  $\eta_s$ , unlike the introduced below parameter  $\eta_{s1}$ , is independent of the small parameters  $\chi$  and  $m^{-1}$ .

The expansion for the transition layer is of the form

$$z(\eta; \chi, m) = \gamma z_9(\eta_9) + \dots; \quad \eta_9 = (\eta - \eta_{s1}) \ln \gamma^{-1}$$

where  $\eta_{s1}$  denotes the root of the algebraic equation  $\alpha(\eta_{s1}) = 1$ . Note that  $\eta_{s1} = \eta_s + o(1)$ . For function  $z_9$  we obtain a problem similar to that for function  $z_7$ . Hence for the charged particle concentration in the transition layer we have in initial variables again formula (3.6) in which subscript  $s1$  is substituted for subscript  $\delta$  (here and below subscripts  $s$  and  $s1$  denote quantities for  $\eta = \eta_s$  and  $\eta = \eta_{s1}$ , respectively).

The expansion for the recombination layer is of the form

$$z(\eta; \chi, m) = \chi z_{10}(\eta) + \dots; \quad \eta < \eta_s$$

and for function  $z_{10}$  we obtain the boundary value problem

$$(d/d\eta)(adz_{10}/d\eta) = bz_{10}^2, \quad \eta = 0; z_{10} = 0; \eta \rightarrow \eta_s, z_{10} \sim 6a_s b_s^{-1}(\eta_s - \eta)^{-2} + \dots \quad (3.9)$$

This problem has generally no analytic solution and must be solved numerically.

**4. Discussion of results.** One of the basic conclusions of this investigation is that the physical picture of deviation from ionization equilibrium near a perfectly catalytic wall, presented in /1/ for the case of ionization by electron impact and recombination only with electrons as the third body, remains essentially the same also in the considered here case of chemical kinetics. This indicates a definite generality of the above picture.

The derived solutions show that in the case of a cold wall ionization and recombination with ion participation does not affect the first approximation solution of the problem. This is easily explained, since in the chemical equilibrium region the specific reaction mechanism does not affect the first approximation solution, while in the unsteady layer region the electron concentration when the wall is cold, is low and reactions with their participation are of minor importance in comparison with reactions with neutral molecule participation (it is assumed that in the unperturbed region the reaction rates of both types are comparable and of order unity). On the other hand, when in the unperturbed region the rate of reactions with electron participation considerably exceeds that of reactions with molecule participation, i.e. when  $c \gg 1$ , this conclusion is not generally valid. In such cases it is necessary to introduce in the problem asymptotic formulation a small parameter linked to the quantity  $c^{-1}$ .

The asymptotic solutions obtained above for various limit cases, using the respective passing to limit, are in agreement. In particular, the second of formulas (2.1) as  $r_w \rightarrow 1$  and  $r_w \rightarrow 0$  are in agreement with the second formulas (1.2) and (3.2), formula (3.5) is in agreement, as  $\alpha_w \rightarrow 0$ , and  $\alpha_w \rightarrow \infty$ , with the second of formulas (3.2) and (3.8), and as  $\eta_s \rightarrow 0$ , problem (3.9) becomes identical with problem (3.7).

These results enable us to formulate the following method for determining the molar concentration derivative of charged particles at the wall as indicated above, this quantity determines the limit particle flux to the wall) for specific conditions. First, we calculate parameter  $\alpha_w$ . If  $\alpha_w \ll 1$ , we use the second of formulas (2.1), and if  $\alpha_w = O(1)$ , formula (3.5). If  $\alpha_w \gg 1$ , we determine the unsteady layer "thickness"  $y_{s1}$ ; if variation of quantities  $nD$  and  $k_{r1}n^3$  over that thickness is small, it is possible to use the second of formulas (3.8), otherwise problem (3.9) is to be solved numerically.

When reactions with neutral molecules are taken into account, a considerable displacement of point  $y_{s1}$  into the region of lower temperatures take place.

As an example, let us consider the simplest model with exponential gas temperature distribution

$$\theta = 1 + (\theta_w - 1)e^{-\eta}$$

We assume that charged and neutral particles interact as Maxwellian molecules /4/, then  $nD \sim T$  and  $a = \theta$ , if  $k_{r1} \sim T^{-1/2}$ , then  $b = \theta^{-1/2}$ . On these assumptions we have

$$\alpha = m\sqrt{\chi} (1 - \theta) \theta^{1/2} e^{m(1-\theta)/(2\theta)}$$

The curve of  $\alpha(\theta)$  calculated by this formula for  $m = 9.3, \kappa = 10^{-6}$  is plotted in Fig.1, where point  $\alpha = 1$  corresponds to  $\theta$  equal 0.411. In the considered model with exponential gas temperature distribution the quantity  $T_{s1}$  is independent of the wall temperature and for  $T_\infty = 2700^\circ\text{K}$  is equal  $1110^\circ\text{K}$ , while the temperature calculated for the same determining parameters using the formulas in /1/ is  $1630^\circ\text{K}$ .

In the case of the hot wall the formulas obtained here are in agreement with the respective formulas in /1/, while in the case of the cold wall they differ.

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