## A THEORY FOR FREEZING OF ELECTRON PROCESSES IN LOW-TEMPERATURE PLASMA JETS

A. B. Vasil'eva and Yu. S. Sayasov

Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, Vol. 9, No. 1, pp. 26-34, 1968

The question of finding the asymptotic values of the relative electron concentrations obtained when the gas temperature and pressure along the streamliner are reduced naturally arises in a number of problems in ionized-gas dynamics. An example of such a problem is that of the flow of a low-temperature plasma in a divergent nozzle. In this case, the velocities of all elementary processes approach zero in proportion to distance from the critical section of the nozzle, due to the marked temperature and pressure drops in the nozzle. Hence, it follows that the relative electron concentration must approach some constant value, which is called the frozen concentration. The study of these processes is of great importance as applied to rocket-engine nozzles [1] and magnetohydrodynamic equipment.

**§1. Statement of the Problem.** In many cases, the equation describing the kinetics of variation of the relative electron concentration x along the streamline can be written as

$$\frac{dx}{dt} = w(t) - \alpha(t) \mathbf{z}^2 \qquad \left( t = \int \frac{dx}{v}, \ x = \frac{q_t}{n} \right), \quad (1.1)$$

where t is the time reckoned along the flow line; z is the coordinate read along the streamline; v is the gas velocity; n is the total number of gas particles per cm<sup>3</sup>; n<sub>e</sub> is the electron concentration. The quantities w and  $\alpha$  are interpreted in relation to the set of elementary processes determining the electron kinetics. For example, for the set of elementary processes

$$A + M \stackrel{h_1}{\underset{h_1}{\longrightarrow}} A^+ + e + M$$
, or  $A + B \stackrel{h_2}{\underset{h_2}{\longrightarrow}} AB^+ + e$  (1.2)

we have

$$w = k_1 x_A n x_M, \quad \alpha = k_1' n^2 x_M, \quad (1.3)$$
$$k_1 = a_1 (T) \exp(-E_1/kT),$$

or

$$w = k_2 x_A x_B n, \quad \alpha = k_2' n,$$
  
 $k_2 = a_2 (T) \exp (-E_2/kT).$  (1.4)

Here,  $k_i$  and  $k'_i$  (i = 1,2) are the rates of the forward and reverse reactions, respectively;  $x_A$ ,  $x_B$ , and  $x_M$  are the relative concentrations of the reacting particles A, B, and M; T is temperature.

The subscript 0 will subsequently denote all values corresponding to the reference time t = 0, which we make correspond to the critical section of the nozzle. Then  $x_0$  can be assumed to coincide with the equilibrium concentration, i.e.,

$$x_0 = \sqrt{w_0 / \alpha_0} . \tag{1.5}$$

If we introduce the electron concentration referred to by its initial value  $\xi = x/x_0$  and let the time t be expressed in units of the characteristic time  $\tau$  of gas

$$\begin{aligned} \lambda d\xi dt &= \phi(t) \exp\left[-G(t)/\varepsilon\right] - \psi(t) \xi^2 & (\lambda = \tau^*/\tau) \\ \tau^* &= \frac{1}{\sqrt{w_0 \alpha_0}}, \quad \phi = \frac{w}{w_0}, \quad \psi = \frac{\alpha}{\alpha_0}, \quad G = \frac{T_0 - T}{T}, (1.6) \\ \varepsilon &= \frac{kT_0}{E_i} (i = 1, 2), \quad \phi(0) = \psi(0) = 1, \quad G(0) = 0, \end{aligned}$$

where  $\tau^*$  is the time for establishment of an equilibrium-concentration.

The functions  $\varphi$ ,  $\psi$ , and G in (1.6) are assumed to be dependent only on the temperature T, and we assume that the temperature dependence of the recombination coefficients has the form  $k'_1 \sim T^{-\nu}$  ( $\nu = 5/2$ for a monatomic gas [2],  $\nu = 7/2$  for nondipole molecules [3],  $\nu = 9/2$  for a gas with dipole molecules [4,5]);  $k'_2 \sim T^{-\nu}$ ,  $1/2 < \nu < 3/2$ . We assume that the coefficients  $k_i$  and  $k'_i$  are related by the principle of detailed balance.

Remarks. The principle equation (1.1) above holds under the following conditions.

1. The effect of electron processes on the gasdynamics of flow is negligible, since the charged-particle concentrations are low under the conditions in question. This allows us to assume that all gasdynamic flow parameters (the distribution of pressure, temperature, and velocity) are given, i.e., to construct the kinetics of the electron processes from those solutions of equations of chemical gasdynamics obtained when electron processes are ignored.

It should be noted, however, that in the special case of a monatomic gas and at the very low temperatures produced when the gas expands, we must take into account the temperature-increase effects resulting from the recombination of electrons and positive ions [6]. In the case of a monatomic gas, final residual ionization in the gas is brought about only by the above-mentioned effect of joining of electron and gasdynamic processes. In a number of cases important in practice, this is not of great significance, since in the region of gas flow that is of interest (for example, up to the nozzle section), the temperature does not drop enough to make this effect significant. We shall ignore this effect below.

2. A plasma in low-temperature jets can be considered quasineutral, i.e., in each elementary volume the number of negatively charged particles equals the number of positively charged particles. This condition is violated only with very high pressure gradients.

3. Under the high-velocity conditions of gasdynamic transport that we are considering, the diffusion of electrons (and, all the more, of heavy particles) can be ignored (the ratio of the velocities of diffusion and gasdynamic electron flows is approximately equal to  $D_e/vL \approx v_e l_e/vL \ll 1$ , where  $D_e$  is the coefficient of ambipolar diffusion,  $l_e$  is the electron mean free path,  $v_e$  is the electron velocity, and L is the characteristic dimension of the nozzle). This allows us to write the kinetic equations as differential equations of the type of (1.1), which represent the balance equation of the velocities of gasdynamic transport and the velocities of elementary processes in which electrons participate for each streamline.

4. The electron temperature can be considered equal to the heavyparticle temperature. For example, in liquid-fuel rocket nozzles, the electron-temperature relaxation time, which is chiefly connected with vibrational-rotational molecular excitation, is very small. In fact, in order of magnitude this time  $\tau_e \approx 1/\sigma$  verw, where  $\sigma$  is the electron-scattering cross section and w is the probability of energy transfer (on the order of kT) in one electron-molecule collision, i.e.,  $w \approx 10^{-2}$ . When  $n \approx 10^{20}$  cm<sup>-3</sup>, we have  $\tau_e \approx 10^{-10}$  sec, i.e.,  $\tau_e$  is usually less than the other effective relaxation times that figure in kinetic equation (1.1). Therefore, in the reaction rates of the elementary processes in which electrons participate, the electron temperature can be considered equal to the heavy-particle temperature.

It should be noted that indications have appeared recently that the electron-temperature relaxation time can, in fact, be considerably higher than that given by the relation  $\tau_e \approx 1/\sigma v_e nw$ . This is due to the fact that electron scattering by molecules can produce long-lived quasistationary rotationally excited states. In some cases, therefore, the electron temperature, even in liquid-fuel rocket nozzles, can differ substantially from the heavy-particle temperature. This does not affect the following discussion, since it leads only to a slight redefinition of the functions  $\varphi$ ,  $\psi$ , and G in (1.6).

A great number of papers have been devoted to the freezing processes described by (1.1), but these papers employ only numerical methods or methods resulting solely in rough estimates [1,7,8].

In contrast, the present paper gives a consistent analytic theory of the freezing processes described by Eq. (1.6). This theory is based on the sole assumption that  $\varepsilon = kT_0/E_i \ll 1$  (i = 1,2), which can usually be considered to be fulfilled. In fact, the ionization energy  $E_i$  is usually several eV, and  $T_0$  does not exceed a few thousands of degrees in the equipment usually employed. As a rule, therefore,  $\varepsilon < 0.1$ .

§2. Mathematical Study of Eq. (1.6). Let us rewrite (1.6) as

$$\lambda \frac{d\xi}{dt} = \varphi(t) \exp\left(-\frac{1}{\varepsilon} \int g \, dt\right) - \psi(t) \,\xi^2, \qquad (2.1)$$

and introduce the derivative g(t) of the function G(t). We examine (2.1) under the initial condition

$$\xi (0) = \xi_0. \tag{2.2}$$

Generally speaking, Eq. (2.1) cannot be integrated in elementary functions. Therefore, we must use asymptotic methods and rely on the presence of the parameters  $\lambda$  and  $\varepsilon$ . Mathematically, we consider the parameter  $\varepsilon$  to be infinitely small, and  $\lambda$  can be either finite or infinitesimal and can have any order of smallness relative to  $\varepsilon$ , i.e.,  $\varepsilon/\lambda$  can approach some finite limit, infinity, or zero.

The problem consists in constructing the asymptotic form of the solution of (2.1) and (2.2) in  $\varepsilon$  and  $\lambda$ , and, in particular, in the asymptotic representation of  $\lim \xi (t, \varepsilon, \lambda) = \xi_{\infty}(\varepsilon, \lambda)$  as  $t \to \infty$ , i.e., the frozen concentration.

The properties of the solutions of (2.1) and (2.2) and the nature of the asymptotic form differ considerably, according to the relations between the parameters  $\varepsilon$  and  $\lambda$ . Therefore, the cases in which  $\varepsilon \leq \lambda$ and  $\varepsilon > \lambda$  will be considered separately. The main text gives a mathematical formulation of the results in the form of asymptotic formulas. Some aspects related to the proof of these formulas are referred to in the supplement. The conditions on  $\varphi$ ,  $\psi$ , and G under which this asymptotic form is valid are listed there.

First case:  $\varepsilon \leq \lambda$ , in which  $\varepsilon \to 0$ , and  $\lambda$  can remain finite or approach zero more slowly than  $\varepsilon$ , or they can be on the same order of smallness as  $\varepsilon$ . In this case, for  $\xi(t,\varepsilon,\lambda)$  we have the uniform asymptotic representation

$$\xi\left(t,\,\varepsilon,\,\lambda\right) = \lambda \left[-\lambda \frac{\psi\left(0\right)}{\varphi\left(0\right)} \frac{C\left(\mathbf{x}\right) I_{\mathbf{0}}\left(s\right) + K_{\mathbf{0}}\left(s\right)}{C\left(\mathbf{x}\right) I_{\mathbf{1}}\left(s\right) - K_{\mathbf{1}}\left(s\right)} \exp \frac{g\left(0\right) t}{2\varepsilon} - \right]$$

$$-\psi(0)t+\Psi(0,t)+O(\varepsilon^2)\Big].$$
 (2.3)

Here,  $I_j(s)$  and  $K_i(s)$  (j = 0,1) are Bessel functions of an imaginary argument,

$$s = 2\varkappa \exp \frac{-g(0)t}{2\varepsilon},$$
  
$$\varkappa^{2} = \frac{\psi(0)\phi(0)}{g^{2}(0)} \frac{\varepsilon^{2}}{\lambda^{2}}, \quad \Psi(a, b) = \int_{a}^{b} \psi(t) dt, \quad (2.4)$$

$$C(\varkappa) = \frac{K_1(2\varkappa) - \xi_0 \sqrt{\psi(0)/\psi(0)} K_0(2\varkappa)}{I_1(2\varkappa) + \xi_0 \sqrt{\psi(0)/\psi(0)} I_0(2\varkappa)}.$$
 (2.5)

The conventional symbol for values that have the order of smallness  $\varepsilon^2$  is  $O(\varepsilon^2)$ . The bound of the remainder term  $O(\varepsilon^2)$  is uniform in t over the entire infinite interval  $0 \le t < \infty$ .

From (2.3) we can derive an expression for the frozen concentration  $\xi_{\infty}(\varepsilon,\lambda)$ , using the asymptotic form of the Bessel functions as  $s \rightarrow \infty$ . This expression has the form (C<sub>E</sub> is Euler's constant):

$$\xi_{\infty}(\varepsilon, \lambda) = \lambda \left[ \Psi(0, \infty) + \frac{2\psi(0)}{\varphi(0)} \varepsilon(C(\varkappa) - C_E - \ln \varkappa) + O(\varepsilon^2) \right]^{-1}.$$
(2.6)

Now let us consider the various possible relationships between  $\varepsilon$  and  $\lambda$ .

a) Let  $\varepsilon \to 0$  and  $\varepsilon/\lambda \to 0$ . In this case,  $\varkappa \to 0$ , the argument of the Bessel functions in (2.6) is small, and, again using the asymptotic form of these functions at small values of the argument, we have, after some calculations,

$$\xi_{\infty} = \lambda \Big[ \Psi(0, \infty) + \frac{\lambda}{\xi_0} - \varepsilon \frac{\Psi(0)}{g(0)} \frac{1}{\xi_0^2} + O\left(\frac{\varepsilon^2}{\lambda}\right) + O\left(\varepsilon^2\right) \Big]^{-1}.$$
(2.7)

If  $\lambda$  is finite,

$$\frac{\lambda}{\lambda/\xi_0 + \Psi(0,\infty)} + \varepsilon \frac{\varphi(0)}{g(0)} \frac{\lambda/\xi_0^2}{(\lambda/\xi_0 + \Psi(0,\infty))^2} + O(\varepsilon^2), \quad (2.8)$$

and if  $\lambda$  is small,

$$\xi_{\infty} = \frac{\lambda}{\Psi(0, \infty)} - \frac{1}{\Psi^{2}(0, \infty)} \left(\frac{\lambda^{2}}{\xi_{0}} - \varepsilon \lambda \frac{\varphi(0)}{g(0)} \frac{1}{\xi_{0}^{2}}\right) + O(\varepsilon^{2}).$$
(2.9)

b) Let  $\varepsilon = \lambda \rightarrow 0$  (the case in which  $\varepsilon$  and  $\lambda$  have the same order of convergence on zero can always be reduced to this case). In this case, formula (2.6) gives

$$\xi_{\infty} = \varepsilon \left\{ \frac{2\psi(0)}{g(0)} \varepsilon \left[ C \left( \frac{\sqrt{\psi(0)\psi(0)}}{g(0)} \right) - C_E - \ln \frac{\sqrt{\psi(0)\psi(0)}}{g(0)} \right] + O(\varepsilon^2) \right\}.$$
(2.10)

Second case:  $\varepsilon > \lambda$ . Mathematically, this case can be described as:  $\lambda/\varepsilon \to 0$ , and  $\varepsilon \ln (\varepsilon/\lambda) \sim 1$ . The latter relation means that  $\lambda$  cannot approach zero too quickly, i.e.,  $\lim \varepsilon \ln (\varepsilon/\lambda) = p$  as  $\varepsilon \to 0$  and  $\lambda \to 0$ . Here, p is any (fixed) number. We assume that  $\epsilon \ln(\epsilon/\lambda) \rightarrow 1$  (since the case of  $p \neq 1$  can be brought to the case of p = 1 by a change of variables). The frozen concentration will be given by the formula

$$\xi_{\infty} = \lambda \left[ \Psi(t^{\circ}, \infty) - \frac{2\psi^{\circ}}{g^{\circ}} \varepsilon \left( C_E + \ln \frac{\sqrt{\varphi^{\circ}\psi^{\circ}}}{g^{\circ}} \right) + o(\varepsilon) \right],$$
(2.11)

where t° is determined by

$$\int_{0}^{t^{\circ}} g \, dt = 2\epsilon \ln \frac{\epsilon}{\lambda} \,. \tag{2.12}$$

The superscript  $^{\circ}$  means that the functions g,  $\varphi$ , and  $\psi$  are taken at the point t = t $^{\circ}$ . The symbol o( $\varepsilon$ ) is conventional for a quantity whose order of smallness is higher than  $\varepsilon$ .

**§3.** Calculation of Frozen Concentrations. On the basis of the general formulas obtained in §2, it is easy to calculate frozen concentrations for various dependences of the gasdynamic values on the z-coordinate. We give the calculation here for gas flow with the constant adiabatic exponent  $\gamma$ . For the flow of combustion products in nozzles of liquid-fuel rockets this assumption does not hold, strictly speaking, since the gas composition varies along the nozzle. Nevertheless, this assumption does not result in substantial errors if as  $\gamma$  we take the quantity pertaining to the critical section of the nozzle. This is because the frozen electron concentration is usually established at small distances from the critical section, at which  $\gamma$  does not have time to change substantially.

Under these assumptions, the relationship between the gasdynamic parameters and the time t is given by the well-known formulas [9]

$$\frac{T_0}{T} = \Phi(M), \quad \frac{v}{v_0} = M \Phi^{-1/4},$$
$$\frac{\rho}{\rho_0} = \frac{n}{n_0} = \Phi^{-1/(\gamma-4)}, \quad \Phi(M) = \frac{(\gamma-4)M^4 + 2}{\gamma+1},$$

where  $\rho$  is the gas density.

As the argument we take the Mach number M, which is related to the coordinate z read along the nozzle axis (and, therefore, to t) by

$$\frac{\rho v}{\rho_0 v_0} = M \Phi^{-\mu} = \frac{S(z_0)}{S(z)} = \frac{S_0}{S}, \quad \mu = \frac{\gamma + 1}{2(\gamma - 1)},$$

where S is the nozzle cross section.

Specific numerical calculations were made when the shape of the nozzle was given by the relation (Fig. 1)

$$z_0 = 0, \quad S = S_0 + k^2 z^2, \quad S = \pi r^2, \quad S_0 = \pi r_0^2$$
  
$$\vartheta = \operatorname{arc} \operatorname{tg} (k/\sqrt{\pi}).$$

Therefore, in the above formulas we must let

$$S/S_0 = 1 \pm \zeta^2, \quad \zeta = z/L, \quad L = r_0/\mathrm{tg}\,\vartheta, \quad \tau = L/v_0$$

In the numerical calculations it was also assumed that the kinetics of an elementary process correspond to the first scheme of (1.2), in which the particle A is an atom of an alkali metal. In this case, the relationship between  $k_1$  and  $k_1$  can, on the basis of the detailed-balance principle, be written as

$$k_1'/k_1 = (2\pi)^{*/2} (\hbar^2/m_c kT)^{*/2} \exp (E_1/kT).$$

In other words, in this case the functions  $\varphi$  and  $\psi$  have the form

$$\varphi = (\underline{U}^{\nu-3/2-1/(\gamma-1)}, \quad \psi = (\underline{U}^{-2/(\gamma-1)+\nu}.$$

If we convert in the formulas of 2 to the independent variable M, we must let

$$dt = \frac{1}{M} \bigoplus^{\nu_{1}} \frac{d_{0}^{*}}{dM} dM,$$

$$g(M) = \frac{dG}{dt} = \frac{d}{dt} \bigoplus (M) =$$

$$= \frac{2(\gamma - 4)M^{4}}{M^{2} - 4} \bigoplus^{(1 - 1)/(\gamma - 1)} (M^{-1}(1 + - 1)^{\frac{1}{2}} - (M \neq 1))$$

$$g(1) = \frac{(\gamma - 4)V^{2}}{V\gamma + 4},$$

$$\forall (t^{\circ}, \infty) = \int_{Y^{\circ}}^{\infty} \bigoplus^{(1)} dt = \int_{M^{\circ}}^{\infty} f(M) dM = F(M^{\circ}, \infty)$$

$$f(M) = \frac{M^{2} - 4}{(\gamma + 1)M^{2}} \frac{\bigoplus^{-1/(\gamma - 1) + 2}}{(M^{-1} \oplus^{0} - 1)^{\frac{1}{2}}} \quad (M \neq 1),$$

$$f(1) = \frac{V^{2}}{V\gamma + 4}.$$

The initial conditions have the form  $\xi_0 = \xi (M = 1) = 1$ .

For convenience, we introduce the following:

$$\varphi' = \frac{\varphi}{\sqrt{\vartheta}}, \quad \psi' = \frac{\psi}{\sqrt{\vartheta}}, \quad \lambda' = \frac{\lambda}{\sqrt{\vartheta}}$$
$$\varepsilon' = \frac{\varepsilon}{g(1)}, \quad g' = \frac{g}{g(1)}$$
$$\vartheta = \exp C_E = 1.781...$$

Then, if we rewrite (2.6) in the new variables for  $\lambda' \geq \varepsilon'$  and (2.11) for  $\varepsilon' > \lambda'$ , we arrive at the following standard working formulas

$$y_{\infty} = \left\{ F(\mathbf{1}, \infty) + 2\varepsilon' \left[ Q\left(\frac{2\varepsilon'}{\lambda' \mathfrak{H}}\right) - \ln \frac{\varepsilon'}{\lambda'} \right] \right\}^{-1} \quad (\varepsilon' \leq \lambda')$$
$$y_{\infty} = \left\{ F(\overline{M}, \infty) - 2\varepsilon' \beta a^{i/\epsilon - 1/2} (\gamma - 1) \ln \beta \right\}^{-1} \quad (\varepsilon' > \lambda')$$
$$\left( y = \frac{\xi}{\lambda} = x \alpha_0 \tau \right) \cdot$$
(3.1)

$$\beta = 2\varepsilon' \ln \frac{\varepsilon'}{\lambda'} a^{\gamma-3/z-1/2(\gamma-1)} b^{-2} (a^{(\gamma+1)/2(\gamma-1)} b^{-3/z} - 1)^{-1/z},$$

$$a = 1 + 2\varepsilon \ln \frac{\varepsilon'}{\lambda'}, \quad b = 1 + 2\varepsilon \frac{\gamma+1}{\gamma-1} \ln \frac{\varepsilon'}{\lambda'}, \quad \overline{M} = b^{1/z},$$

$$Q(z) = \frac{K_1(z) - K_0(z)}{I_1(z) + I_0(z)}.$$



Fig. 2. Graphs of  $y_{\infty}$  as a function of  $1/\lambda$  for  $\nu = \frac{9}{2}$  and  $\gamma = 1.25$  (curves 1, 2, and 3) and  $\nu = \frac{9}{2}$  and  $\gamma = 1.15$  (curves 4, 5, and 6).

With (2.1), we calculated  $y_{\infty}$  as a function of  $\lambda$  for the following four combinations of the parameters  $\nu$  and  $\gamma$ :

(1) 
$$v = \frac{7}{2}, \gamma = \frac{9}{7},$$
 (2)  $v = \frac{9}{2}, \gamma = 1.25$   
(3)  $v = \frac{9}{2}, \gamma = 1.20;$  (4)  $v = \frac{9}{2}, \gamma = 1.15$ 

For each combination, calculations were made for  $\varepsilon = 0.02$ , 0.04, and 0.06. Combination (1) corresponds to ionization in a gaseous medium of nondipole diatomic molecules similar to N<sub>2</sub> under the assumption that vibrational degrees of freedom are excited. Combinations (2), (3), and (4) correspond to ionization in a gas of dipole molecules similar to H<sub>2</sub>O. The calculated values are given in the table and in Fig. 2. To check asymptotic formulas (3.1), Eq. (2.1) was integrated exactly on a Strela computer for  $\nu = 7/2$ ,  $\gamma = 9/7$ , and  $\varepsilon = 0.04$  and for  $\lambda = 10$ , 1, 0.2, 0.1, 0.02, and 0.01. The values of  $y_{\infty}$  so obtained are in good agreement with the values of  $y_{\infty}$  given by (3.1). We thank E. K. Gutkovich, E. V. Chebotaev, and V. M. Martynova for making the calculations.

Figure 2 can be used to make specific calculations of the frozen concentration for all cases of practical interest. As an example, we shall calculate the frozen concentrations in the combustion products of a liquid-fuel rocket engine. In this case, the main combustion product is  $H_2O$ , and, according to [4], the first reaction of (1.2), where M is an  $H_2O$  molecule, can be considered as the principal ionization process. With the expression for the recombination coefficient  $k_1$  given in [4,5], we have

$$\alpha = \alpha_0 \Phi^{0/2-2/(\gamma-1)}, \quad \alpha_0 = k_1' n_0^2 x_M, \quad k_1' = 6.3 \cdot 10^{-12} T^{-0/2}.$$

We assume that the water concentration does not vary substantially along the nozzle. On the other hand,  $1/\lambda = \alpha_0 \tau x_0 = \alpha_0 \tau (x_A/k_1 n_0)^{1/2}$ . If, in particular, we take  $T_0 = 2500^{\circ}$  K,  $n_0 = 10^{20}$  cm<sup>-3</sup>,  $\tau = 10^{-3}$  sec, and  $x_M = 0.5$ , and if we assume that the primary process is the ionization of sodium, i.e., the particle A is a Na atom, for which  $E_1 = 5.14$  eV, then  $\varepsilon = 0.04$ ,  $\alpha_0 \tau = 1.1 \cdot 10^{10}$ , and  $1/\lambda = 2.3 \cdot 10^5 (x_A)^{1/2}$ . According to Fig. 2, when  $x_A = 10^{-8}$  and  $x_0 = 2 \cdot 10^{-9}$ , we obtain for this example  $1/\lambda = 23$ ,  $x_{\infty} \alpha_0 \tau = 3$ , and, finally,  $x_{\infty} = 2.7 \cdot 10^{-10}$ .

We note also that on the basis of the general formulas of \$2 a number of important qualitative conclusions can be drawn about the behavior of frozen concentrations as a function of the various parameters. Particularly noteworthy is the fact the dependence of the frozen concentration  $x_{\infty}$  on the concentration of the easily ionized impurity  $x_A$  has (other conditions being given) an entirely different nature at small  $x_A$ , defined by the inequality

$$1/\lambda = \alpha_0 \tau \sqrt{x_A/k_1 n_0} < 1/8$$

and at rather large  $x_A$ , defined by the inequality  $1/\lambda > 1/\epsilon$ .

In the former case, the frozen concentration  $x_{\infty}$  depends considerably on  $x_A$  (see (2.8), for example). On the other hand, as is immediately clear from Fig. 2, this dependence is very weak when  $1/\lambda > 1/\epsilon$ .

In other words, the condition  $1/\lambda = 1/\varepsilon$ , i.e.,

$$E_1 / kT_0 = \sqrt{w_0 \alpha_0 \tau},$$

determines some critical value of  $x_{A}^{*}$ , beginning with which the frozen concentration does not vary substantially. For the above numerical example, this critical value is  $x_{A}^{*} \approx 10^{-8}$ .

In conclusion, let us compare the exact formulas (2.6) and (2.11) derived in this paper for frozen concentrations with the approximate method (see, for example, [6], p. 447) usually used to determine  $x_{\infty}$ . According to this method, at  $0 \le t \le t_1$  the concentration x, which is determined by Eq. (1.1), has a quasi-stationary variation, i.e.,  $x = x_{eq} = (w/\alpha)^{1/2}$ , while at  $t \ge t_1$  it is obtained by our integrating (1.1), in which w = 0 is assumed, i.e., according to this estimate,

$$\boldsymbol{x}_{\infty} = \boldsymbol{x}_{eq}\left(t_{1}\right) / \left(1 + \boldsymbol{x}_{eq}\left(t_{1}\right) A\left(t_{1}, \infty\right)\right), \qquad A\left(t_{1}, \infty\right) = \int_{t_{1}}^{\infty} \alpha \, dt$$

The time  $t_1$  is dictated by the condition that the deviation  $\delta x$  of the concentration from quasi-stationary, which is given by the formula  $\delta x = -(1/2\alpha) d \ln x_{eq}/dt$ , be approximately equal to  $x_{eq}$ .

Since the frozen concentration  $x_{\infty}$  is usually appreciably less than  $x_{eq}(t_1)$ , i.e.,  $x_{eq}(t_1)A(t_1,\infty) \gg 1$  and, therefore,  $x_{\infty} \approx 1/A(t_1,\infty)$ , while, on the other hand, the value of  $t_1$  introduced here coincides approximately, as is easily shown, with  $\tau t^{\circ}$ , where t° is determined by (2.12), it follows that formula (2.11), if the term proportional to  $\varepsilon$  is ignored, gives a result that agrees in order of magnitude with that obtained by the estimate usually used, which is given in [1,6,8] and which is valid when  $\lambda < \varepsilon$ . However, if  $\varepsilon < \lambda$ , as can be seen from formula (2.6) the expression for the frozen concentration differs greatly from that given by the above-mentioned approximate method, and in this case its use is entirely unjustified.

\$4. Supplement. We indicate the main aspects of the proof of asymptotic formulas (2.3) and (2.11).

First, let us list the main assumptions about those values in (2.1) for which the mathematical theory was developed. These assumptions are fairly natural from the point of view of physics.

1) The quantities  $\varphi(t)$ ,  $\psi(t)$ , and g(t) are positive and continuously differentiable in  $0 \le t < \infty$ . 2) The quantity  $\psi(t)$  is uniformly bounded

Values o	f y∞	as a	Function	of	$1/\lambda$	for	Various	Values	of $\nu$ ,	γ,	and	ε
----------	------	------	----------	----	-------------	-----	---------	--------	------------	----	-----	---

Table

1/2.	0.1	1	5	10	50	100
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	7         0.53           77         0.56           77         0.51           77         0.54           77         0.54           77         0.58           7         0.54           7         0.56           7         0.58           7         0.64           7         0.68           7         0.69           7         0.69           7         0.68           7         0.69           7         0.69           7         0.69           7         0.82	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccc} 1.65 \\ 1.81 \\ 2.04 \\ 1.44 \\ 1.62 \\ 1.83 \\ 1.95 \\ 2.34 \\ 2.93 \\ 2.52 \\ 3.50 \\ 5.32 \end{array} $	$ \begin{vmatrix} 2.04 \\ 2.62 \\ 3.28 \\ 1.79 \\ 2.29 \\ 2.83 \\ 2.71 \\ 4.03 \\ 5.78 \\ 4.45 \\ 7.96 \\ 14.78 \end{vmatrix} $	$\begin{array}{c c} 2.24\\ 3.01\\ 3.88\\ 1.96\\ 2.60\\ 3.30\\ 3.11\\ 4.94\\ 7.37\\ 5.11\\ 10.85\\ 21.55\end{array}$

along with its derivative and approaches zero as  $t \to \infty$  as a certain power  $1/t^{\alpha}$  ( $\alpha > 1$ ) (we write:  $\psi(t) \sim 1/t^{\alpha}$ ), so that

$$\Psi(0, \infty) = \int_{0}^{\infty} \Psi(t) dt.$$

We note that formula (2.3) remains valid when  $\alpha \leq 1$  (for example, in the case of ionization in a monatomic-gas medium, when  $\vartheta = 5/2$  and  $\gamma = 5/3$ ). In this case, the frozen concentration is zero, since  $\Psi(0, \infty) = \infty$  (see remark 1 in §1). 3) The quantity  $\varphi(t) \sim t^{P}(p \geq 0)$  and the quantity  $\varphi'(t) \sim t^{p-1}$  as  $t \to \infty$ . 4) The quantity  $g(t) \sim c^{-q}$  ( $1 \leq q < 1$ ) as  $t \to \infty$ .

First case:  $\varepsilon \leq \lambda$ . Let us convert in (2.1) to the variable V =  $\lambda/\xi$ , whose equation has the form

$$\frac{dV}{dt} = -\frac{\Psi(t)}{\lambda^2} V^2 \exp\left(-\frac{1}{\varepsilon} \int_0^t g \, dt\right) + \Psi(t),$$

$$V(0) = \frac{\lambda}{\xi_0} \cdot \frac{1}{\varepsilon} \int_0^t g \, dt$$
(4.1)

Let us compare with this equation the equation obtained from it when we let t = 0 in  $\varphi$ ,  $\psi$ , and g:

$$\frac{dU}{dt} = -\frac{\varphi(0)}{\lambda^2} U^2 \exp\left(-\frac{\varphi(0)}{\varepsilon}t\right) + \psi(0), \qquad (4.2)$$
$$U(0) = \frac{\lambda}{\xi_0}$$

Theorem 1: For V there is an asymptotic representation uniform in  $0 \le t < \infty$ ;

$$\Psi(t) = \{U(t) - \psi(0) t + \Psi(0, t)\} + \delta,$$

$$\Psi(0, t) = \int_{0}^{t} \psi(t) dt$$
(4.3)

where  $|\delta| < C\epsilon^2$  (C is a constant independent of  $\lambda$  and  $\epsilon$  when  $\lambda$  and  $\epsilon$  are sufficiently small).

The proof of this theorem consists of writing a differential equation for the difference  $\Delta = V - (U - \psi(0)t + \Psi(0,t))$ , of subsequent conversion to an integral equation, and ob obtaining from the latter an inequality for  $\Delta$  by the so-called method of a priori bounds. Since we cannot give this proof here, we shall briefly explain the idea of approximate replacement of V by the expression  $U - \Psi(0)t + \Psi(0,t)$ . It is intuitively clear that  $\alpha = V - \Psi(0,t)$  and  $\beta = U - \psi(0)t$  must be similar values. In fact,

$$\frac{d\alpha}{dt} = -\frac{\varphi(t)}{\lambda^2} V^2 \exp\left(-\int_0^t \frac{g \, dt}{e}\right),$$
$$\frac{d\beta}{dt} = -\frac{\varphi(0)}{\lambda^2} U \exp\left(-\frac{g(0) t}{e}\right).$$

Yet in view of the smallness of  $\varepsilon$  (sharp decay of the exponent) in the preexponential factor and in the exponent itself, the quantities can be replaced by their initial values without substantial error. Then the right-hand sides of the equations for  $\alpha$  and  $\beta$  will have, respectively, the forms

$$-\frac{\varphi(0)}{\lambda^2} V^2(0) \exp\left(-\frac{g(0)t}{\varepsilon}\right),$$
$$-\frac{\varphi(0)}{\lambda^2} U^2(0) \exp\left(-\frac{g(0)t}{\varepsilon}\right),$$

and since  $V(0) = U(0) = \lambda/\xi_0$ , then  $da/dt \approx d\beta/dt$ , i.e.,  $\alpha \approx \beta$ , and this is actually expressed in (4.3).

The approximate expression (4.3) of V in terms of U is rational, because Eq. (4.2) is integrated in Bessel functions of an imaginary argument, that is, U has the form

$$U = -\lambda \sqrt{\frac{\overline{\psi(0)}}{\overline{\phi(0)}}} \frac{CI_0(s) + K_0(s)}{CI_1(s) - K_1(s)} \exp \frac{g(0)}{2s} t, \qquad (4.4)$$

where s and C are given by formulas (2.4) and (2.5). If we substitute (4.4) into (4.3) and consider that  $\xi = \lambda/V$ , we arrive at uniform asymptotic representation (2.3) for  $\xi(t, s, \lambda)$ .

Second case:  $\lambda < \varepsilon$ ,  $\varepsilon \ln(\varepsilon/\lambda) \sim 1$ . The following procedure can be used in this case. Beginning with time  $t = t^{\circ}$ , where  $t^{\circ}$  is defined by (2.12), we introduce the new function  $\eta = (\varepsilon/\lambda)\xi$ . Then Eq. (2.1) is written as

$$\varepsilon \frac{d\eta}{dt} = \varphi(t) \exp\left(-\frac{1}{\varepsilon} \int_{t^{\circ}}^{t} g dt\right) - \psi(t) \eta^{2}.$$
(4.5)

Equation (4.5) will, in essence, be an equation of the type  $\lambda = \varepsilon$  already examined, provided that we take  $t = t^{\circ}$  as the initial point. Therefore, all the preceding reasoning can be applied to Eq. (4.5), i.e., we can use the fact that when  $t \ge t^{\circ}$  the main role in the expression exp (-1/ $\varepsilon$  g dt) is played by times that are close to t°, and, therefore, the solution can be expressed in terms of the solution of the auxiliary equation obtained from (4.5) if in it we let

$$\begin{aligned} \varphi\left(t\right) &= \varphi\left(t^{\circ}\right) = \varphi^{\circ}, \quad \psi\left(t\right) = \psi\left(t^{\circ}\right) = \psi^{\circ}, \\ &\int_{t^{\bullet}}^{t} g \ dt = g \ (t^{\circ}) \ (t - t^{\circ}) = g^{\circ} \ (t - t^{\circ}). \end{aligned}$$

In this case, however, a question arises about the formulation of the modified initial condition  $\eta(t^{\circ}) = \eta_0$  for Eq. (4.5). Without giving its derivation, the final result is

$$\eta_0 = \left(\frac{\Phi^{\circ}}{\Psi^{\circ}}\right)^{1/2} \frac{K_1(2 \ V \overline{\Phi^{\circ} \Psi^{\circ}} / g^{\circ})}{K_0(2 \ V \overline{\Phi^{\circ} \Psi^{\circ}} / g^{\circ})}.$$

If we reproduce under this initial condition all of the reasoning that led to (4.3) and consider that  $\lambda = \varepsilon$ , we obtain (2.11) for  $\xi_{\infty}$ .

## REFERENCES

1. A. Q. Eshenroeder, "Ionization nonequilibrium in expanding flows," ARS Journal, vol. 32, no. 1, 1962.

2. L. P. Pitaevskii, "Electron recombination in a monatomic gas," Zh. eksperim. i teor. fiz., vol. 42, no. 5, 1964.

3. F. I. Dalidchik and Yu. S. Sayasov, "Electron recombination in molecular gases," Zh. eksperim. i teor. fiz., vol. 49, no. 7, 1965.

4. A. N. Hayhurst and T. M. Sugden, "The ionization processes associated with metallic additives in flame gases," Tr., IUPAC, 1965.

5. F. I. Dalidchik and Yu. S. Sayasov, "On electron recombination in a gas of dipole molecules," Zh. eksperim. i teor. fiz., vol. 52, no. 7, 1967.

6. Ya. B. Zel'dovich and Yu. P. Raizer, Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena [in Russian], Izd, Nauka, 1966.

7. K. N. Bray, "Atomic recombination in a hypersonic wind tunnel nozzle," J. Fluid Mech., vol. 6, no. 1, 1959.

8. Yu. S. Sayasov, "Theory of freezing of ionization processes in expanding gas jets," Dokl. AN SSSR, vol. 162, no. 4, 1965.

9. L. D. Landau and E. M. Lifshits, Mechanics of Continuous Media [in Russian], Fizmatgiz, 1953.

10 September 1966