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Abstract

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THEORY OF THE FREEZING OF IONIZATION PROCESSES IN GAS JETS

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The kinetics of ionization processes accompanied by recombination of electrons e and positive ions A^+, AB^+ (of the type $A + M \underset{k_0'}{\overset{k_0}{\rightleftarrows}} A^+ + e + M$, $A + B \underset{k_1'}{\overset{k_1}{\rightleftarrows}} AB^+ + e$) in expanding gas jets is usually characterized by the following qualitative features. In the initial stage of expansion, while the temperatures are sufficiently high, the effective time for establishing ionization equilibrium $\tau = 1/\sqrt{k_0 k_0' n^2 n_A}$ or $\tau = 1/\sqrt{k_1 k_1' n_A n_B}$ (n_A, n_B, n are, respectively, the absolute concentrations of particles A and B and the total number of particles per 1 cm^3) is smaller than the characteristic time of gas flow L/v (L is an effective dimension, v the gas velocity), i.e., equilibrium has time to be established and the electron concentrations are close to equilibrium. Subsequently, because of the fall in temperature and the rapid decrease in the ionization rate constants k_0 or k_1, the opposite situation arises: the ionization rate becomes vanishingly small, equilibrium no longer has time to be established, and the change in the relative concentration of electrons occurs only at the expense of recombination, whose rate also rapidly decreases in connection with the decrease in the total particle density n. As a result, the relative concentration of electrons $x = n_e/n$ tends to a certain constant value x_f, i.e., what is called freezing of the ionization process occurs.

The kinetics of ionization for $x \ll 1$ is described by the equation

$$dx/dt = w - \alpha x^2, \tag{1}$$

where $w = k_0 n_A$ or $k_1 n_A n_B / n$; $\alpha = k_0' n^2$ or $k_1' n$ (k_0, k, k_1' are specified in units of cm^3/sec); $t = \int_0^l dl/v(l)$, l is the coordinate measured along the streamline; $\alpha \to 0$, $w \to 0$ as $t \to \infty$. The phenomenon of freezing means, in mathematical terms, that as $t \to \infty$, $x \to x_f = \text{const} > 0$. The course of the ionization curves $x = x(t)$ and the values of the frozen concentrations x_f are usually found by numerical integration of equation (1), see, for example, (^{1}). In the present note a general analytical method is set forth for finding x_f and $x(t)$.

Using the change of variable $s = \int_t^\infty \alpha\, dt$, the solution of equation (1) can be written in the form $x = -d \ln y/ds$, where y is the solution of the equation

$$d^2y/ds^2 = x_p^2(s)y, \tag{2}$$

$x_p = \sqrt{w/\alpha}$ has, obviously, the meaning of the equilibrium concentration x. In the initial stage of gas expansion (t small, x_p large), particular solutions of equation (2), $y_{1,2}$, can be represented with the aid of the WKB approximation known from quantum mechanics,

$$y_{1,2} = x_p^{-1/2} \exp\left[\int_{s_0}^{s} x_p\, ds\right], \qquad s_0 = \int_0^\infty \alpha\, dt. \tag{3}$$

According to (3), the solution of (1) has the form

$$\begin{aligned} x &= x_p \frac{\exp\left[-\int_{s_0}^{s} x_p\, ds\right] - C\exp\left[\int_{s_0}^{s_0} x_p\, ds\right]}{\exp\left[-\int_{s_0}^{s} x_p\, ds\right] + C\exp\left[\int_{s_0}^{s} x_p\, dp\right]} + \frac{1}{2}\frac{d}{ds}\ln x_p(s) \\ &= x_p(t)\frac{\exp\left[\int_0^t \frac{dt}{\tau}\right] - C\exp\left[-\int_0^t \frac{dt}{\tau}\right]}{\exp\left[\int_0^t \frac{dt}{\tau}\right] + C\exp\left[-\int_0^t \frac{dt}{\tau}\right]} - \frac{1}{2\alpha}\frac{d}{dt}\ln x_p(t); \qquad \tau = \frac{1}{\sqrt{w\alpha}}, \end{aligned} \tag{4}$$

where C is a constant chosen from the initial conditions at $t = 0$. For

$$\int_0^t \frac{dt}{\tau},$$

i.e., for $t > \tau(0)$, in (4) one may neglect the terms containing $\exp \int_{s_0}^{s} x_p ds$, and, consequently, in the region $t > \tau(0)$ the solution has the form

$$x = x_p\left(1 + \frac{1}{2x_p}\frac{d\ln x_p}{ds}\right) = x_p\left(1 - \frac{1}{2}\tau\frac{d\ln x_p}{dt}\right). \tag{5}$$

According to (5), appreciable deviations from the equilibrium distribution $x = x_p$ begin in the region $s \sim s_k$, where $\tau \sim 1/\frac{d\ln x_p}{dt}$, i.e., where the time of approach to equilibrium τ becomes comparable with the quantity $1/\frac{d\ln x_p}{dt}$, which has the order of the effective flow time of the gas.

Another asymptotic distribution $x = x(t)$ is obtained from (2) for $s \to 0,\ t \to \infty$, when in (2) $x_p^2 y \to 0$, i.e., $y = A - Bs$, hence

$$x = \frac{B}{A - Bs} = \frac{x_f}{1 - x_{fs}}, \qquad x_f = \frac{B}{A}. \tag{6}$$

The principal result of the present work consists in establishing the connection between the asymptotic distributions (5) and (6). This can be done by means of the method of comparison equations (see ($^{2-4}$), and also the work (^{5}), in which this method is formulated for a case analogous to that considered below). As applied to the problem under consideration, the method of comparison equations is as follows. Let $s = s_k$ be a certain critical value of s, beginning with which appreciable deviations from equilibrium take place, i.e., s_k is determined according to (5) by the condition

$$d \ln x_p / ds = a x_p, \qquad a \sim 1. \tag{7}$$

For $s \sim s_k$, represent the quantity $x_p(s)$ in the form $x_p = x_p(s_k) \exp[-\beta(s_k - s)]$ (this can always be done in the range of variation of s satisfying the condition $(T_k - T)/T \ll 1$, where T_k is the temperature corresponding to $s = s_k$). According to the general rules of the method of comparison equations (see (^{5})), the solution of equation (2), uniformly valid from $t \gtrsim \tau(0)$ up to values $s \sim s_k$, for which the approximation $x_p = x_p(s_k) \exp[-\beta(s_k - s)]$ holds, may be written in the form

$$y = \frac{\varphi^{1/2}}{x_p^{1/2}} K_0(\varphi), \qquad \text{i.e.} \quad x = -\frac{d}{ds} \lg \left[\frac{\varphi^{1/2}}{x_p^{1/2}} K_0(\varphi) \right], \qquad \varphi = \int_0^s x_p \, ds; \tag{8}$$

$K_0(\varphi)$ is the Macdonald function. As $t \to 0$, φ is large and $K_0 \approx \sqrt{\pi/2\varphi}\, e^{-\varphi}$, i.e.

$$y = x_p^{-1/2} \exp\left[-\int_0^s x_p \, ds \right].$$

Thus, the expression defined by (8), as $t \to 0$, goes over into (5). On the other hand, in the region $s \sim s_k$,

$$\varphi = x_p(s_k) \frac{1}{\beta} \exp[-\beta(s_k - s)],$$

i.e., in the region $s \sim s_k$,

$$x = -\frac{d}{ds}\ln K_0(\varphi). \tag{9}$$

As $s \to 0$, $\varphi \to 0$, $K_0 \approx \ln 2/\gamma\varphi$ (γ is Euler' s constant), i.e., in this region it follows from (9) that

$$x = \frac{\beta}{\ln[2\beta/\gamma x_p(s_k)] + \beta(s_k - s)}. \tag{10}$$

Expression (10) coincides with the asymptotic distribution (6), i.e., it gives the desired concentration distribution in the quenching region. According to (10), the quenched concentrations (corresponding to $s = 0$) are given by the expression

$$x = x_p(s_k)/(1 + x_p(s_k)s_k) \tag{11}$$

In (11) it has been assumed that the quantity $\beta/\ln\dfrac{2\beta}{\gamma x_p(s_k)}$ is of the same order as $x_p(s_k)$, on the basis of the following considerations: taking

$$x_p = A(T)\exp[-I/2T]$$

(I is the ionization potential in degrees), by definition we have

$$\beta = -\left.\frac{I}{2}\frac{d}{ds}\frac{1}{T}\right|_{s=s_k}.$$

On the other hand,

$$\frac{d\ln x_p}{ds} \approx -\frac{I}{2}\frac{d}{ds}\frac{1}{T}.$$

Hence, on the basis of (7), we obtain $\beta \approx x_p(s_k)$. The quantity $x_p(s_k)$ in (11) is determined by the indicated method to within a factor of order unity. On the other hand, the quantity s_k is determined by condition (7) with logarithmic accuracy, i.e., in effect uniquely. Indeed, taking $x_p = A\exp[-I/2T]$, one can rewrite (7) in the form

$$\frac{I}{2T} = \ln\left[\ln\frac{I}{2A}\frac{d}{ds}\left(\frac{1}{T}\right)\right] + \ln a.$$

Since $I/2T \gg 1$, i.e.

$$\ln\left[\ln\frac{I}{2A}\frac{d}{ds}\left(\frac{1}{T}\right)\right]\gg 1,$$

$\ln a$ may be neglected. Thus, the equation determining s_k can be written in the form

$$\frac{I}{2T(s_k)}=\ln\left[\ln\frac{I}{2A(s_k)}\frac{d}{ds}\frac{1}{T(s_k)}\right]. \tag{12}$$

It should be emphasized that in most cases $x_p(s_k)\gg 1/s_k$ (in other words, the concentration in the critical region $s\sim s_k$ is much greater than the quenched concentration x_f). Therefore, under these conditions

$$x_f=1/s_k, \tag{13}$$

where s_k is determined by equation (12), i.e., x_f is determined quite uniquely.

We shall now apply the general formulas (8), (12), (13) to the analysis of the quenching of the thermoionization process

$$\mathrm{A}+\mathrm{M}\rightleftarrows\mathrm{A}^{+}+e+\mathrm{M}$$

in a gas characterized by a constant adiabatic exponent γ and flowing in an expanding conical nozzle. This process was investigated in work (1) by numerical integration of equation (1); the results of that work we shall use for comparison with our general formulas. Accor—

but under the indicated conditions (1)

$$\alpha=\frac{A_i}{t^p},\quad w=\frac{B_i}{t^q}\exp[-gt],$$

where t is dimensionless time (the beginning of the nozzle, according to (1), corresponds to $t=1.5$), $g=I/2T_i$; A_i, B_i are dimensionless parameters determined by the initial temperature T_i and pressure; $p=2/(\gamma-1)-3/2,\ q=1(\gamma-1)$.

Passing to the variable

$$s=\int_t^\infty\alpha\,dt=\frac{A_i}{p-1}\frac{1}{t^{p-1}},$$

one has, in the case under consideration,

$$x_p=\frac{\chi}{s^\lambda}\exp\left[-\frac{\rho}{s^\mu}\right],\quad \mu=\frac{1}{p-1},\quad \lambda=\frac{p-q}{2(p-1)},$$

$$\chi = \sqrt{\frac{B_i}{A_i}} \left(\frac{A_i}{p-1} \right)^{\lambda}, \quad \rho = \frac{g}{2} \left(\frac{A_i}{p-1} \right)^{\mu}.$$

We note that in the special case $\mu = 1, \ \lambda = 2$, equation (2) has the exact solution ((6), p. 112)

$$y = sK_0 \left(\frac{\chi}{\rho} \exp\left[-\frac{\rho}{s} \right] \right) \to s \ln \left(\frac{2\rho}{\gamma\chi} \exp\left[\frac{\rho}{s} \right] \right) = \rho - s \ln \frac{\gamma\chi}{2\rho} \quad \text{as } s \to 0.$$

Thus, in the quenching region, for this example we have

$$x = \frac{\frac{1}{\rho} \ln \frac{\gamma\chi}{2\rho}}{1 - s\frac{1}{\rho} \ln \frac{\gamma\chi}{2\rho}}. \tag{14}$$

According to (14), the quenched concentration is given by the formula

$$x_f = \frac{1}{\rho} \ln \frac{\gamma\chi}{2\rho}. \tag{15}$$

Let us now find the quenched concentrations from the general formulas (12), (13). Equation (12), in the case under consideration, is written in the form

$$-\frac{\rho}{s_k^{\mu}} = \ln \frac{\chi}{\mu\rho} + (1 + \mu - \lambda) \ln s_k. \tag{16}$$

In the special case $\mu = 1, \ \lambda = 2$, it gives the solution

$$x_f = \frac{1}{s_k} = \frac{1}{\rho} \ln \frac{\chi}{\rho}, \tag{17}$$

which agrees with the exact solution (15) to within a quantity of order

$$\ln \frac{2}{\gamma} \Big/ \ln \frac{\chi}{\rho} \sim \frac{T(s_k)}{I}.$$

The results of calculations of the quantities x_t and of the time dependence $x = x(t)$, which we carried out using formulas (8), (13), and (16), proved to be in good agreement with the results of numerical integration of equation (1), carried out in work (1) under the conditions $T_i = 3100^{\circ}\mathrm{K}$, $g = 16.1$, $\gamma = 1.28$.

In conclusion, we note that the method developed here can also be used to investigate quenching processes of chemical dissociation reactions of the type $A + M \rightleftarrows B + C + M$, likewise described by equation (1).

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Note: Figure translations are in progress. See original paper for figures.