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VIBRATIONAL AND CHEMICAL KINETICS EQUATIONS IN A COMPLEX GAS MIXTURE

O. V. Skrebkov

As a result of the development of computer engineering, as well as the achievements of experimental and theoretical science on the kinetics of elementary processes in gas systems, as a research instrument supplementing, or even replacing completely, the tedium of experiment in the last two decades, computation of complex mixtures in composition and gasdynamics are widespread. In particular, a broad class of problems exists for the analysis of multicomponent gas mixture flow which requires taking account jointly of the chemical reaction kinetics and the vibrational energy exchange processes. On the basis of utilizing simplifying assumptions in the majority of problems of this kind, the kinetic-equations are formulated in the form of macroscopic equations for the concentration and the mean vibrational energies of the components or separate vibrational degrees of freedom (modes) (see [1, 2], e.g.). However, knowledge of the population of the vibrational levels of the separate molecular components of the mixture that changes as a result of chemical and vibrational interaction with a large number of other components can have value, in principle, in solving a number of problems (for instance, in modeling working media flows in chemical lasers [3]). Sequential formulation of the kinetic equations in the form of population balance equations for the vibrational states of a large number of complex mixture components, without already speaking about the extreme tedium of solving them in conjunction with the gasdynamics equations, evidently simply have no practical meaning because of the absence of detailed information about the quantitative characteristics of a very large number of elementary processes required in this case.

Such a formulation of the kinetic equations, in which one group of chemical components and vibrational states is considered microscopically (i.e., in the form of population balance equations) and the other macroscopically (i.e., in the form of equations for the mean vibrational energies and concentrations), results in a significant reduction in the vibrational states taken into account and in their associated elementary processes as compared with the sequential microscopic approach. An example is given in this paper of such a combined formulation of the kinetic equations. Here the subsystem considered microscopically is a mixture of diatomic gases, anharmonic oscillators, chemically and vibrationally interacting mutually and with other polyatomic components comprising the subsystem considered macroscopically, in the general case.

1. KINETIC PROCESSES AND ASSUMPTIONS

The following simplifying assumptions are used in formulating the kinetic equations: a) The chemical reactions do not spoil the Maxwell distribution; b) the rotational degrees of freedom are in equilibrium with the translational; c) each kind of vibrations (mode) of the molecules considered macroscopically is modeled by a harmonic oscillator with infinitesimal characteristic time of VV-exchange within the mode, and the vibrational temperature T_k is used as a measure of the mean energy of such a mode (the k-th, e.g.); d) the molecules of the components considered microscopically are modeled by Morse oscillators.
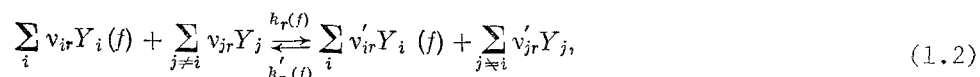
The following are postulated as possible elementary processes.

1. Integrated or macroscopic chemical reactions resulting in a change in the component concentration as a whole

$$\sum_{j=1}^{N} v_{jr} Y_j \underset{k'_r}{\overset{k_r}{\rightleftharpoons}} \sum_{j=1}^{N} v'_{jr} Y_j, \tag{1.1}$$

where Y_j is the j-th chemical component, v_{jr}, v'_{jr} are stoichiometric coefficients of the j-th component in the r-th reaction, N is the total number of chemical mixture components, and k_r, k'_r are rate constants of the r-th chemical reaction in the forward and reverse directions.

2. Detailed or microscopic chemical reactions (with the participation of components considered microscopically):

$$\sum_{i} v_{ir} Y_i(f) + \sum_{j\neq i} v_{jr} Y_j \underset{k'_r(f)}{\overset{k_r(f)}{\rightleftharpoons}} \sum_{i} v'_{ir} Y_i(f) + \sum_{j\neq i} v'_{jr} Y_j, \tag{1.2}$$

where $Y_i(f)$ is the i-th chemical component in the vibrational state f, and $k_r(f)$, $k'_r(f)$ are rate constants of the r-th microscopic chemical reaction in the forward and reverse directions. It is assumed that one of the stoichiometric coefficients v_{ir} or v'_{ir} of the i-th component, considered microscopically, equals zero.

3. Integrated or macroscopic vibrational relaxation processes of the components (or modes) considered macroscopically and modeled by harmonic oscillators

$$\{v_m; v_n\} \overset{P_{ji}^{(q)}}{\rightleftharpoons} \{v_m - l_{mq}; v_n + l_{nq}\}, \tag{1.3}$$

in which a diminution in the vibrational quantum numbers v_m by l_{mq} occurs during the collision of molecules of the j-th and i-th species in the modes m while v_n increases by l_{nq} in the modes n. By virtue of utilization of the haromine oscillator model for modes taking part in a q-th process of type (1.3), the probability of such a process is characterized uniquely by the probability of the appropriate transition between the lowest states [1], i.e.,

$$P_{ji}^{(q)} = P_{ji} \begin{Bmatrix} l_{mq}, & 0 \\ 0, & l_{nq} \end{Bmatrix}.$$

4. Detailed or microscopic vibrational relaxation processes during molecule—anharmonic oscillator collisions

$$\{f; s\} \overset{P_{ij}^{(q)}(f,s)}{\rightleftharpoons} \{f - l_{iq}; s + l_{jq}\}, \tag{1.4}$$

where $P_{ij}^{(q)}(f, s) = P_{s,s+l_{jq}}^{f,f-l_{iq}}$ is the probability of a q-th process of type (1.4) in which l_{iq} quanta of a molecule of the species i in the vibrational state before a collision f is exchanged by l_{jq} quanta of a molecule of the species j in the vibrational state s before the collision.

5. Detailed or microscopic vibrational relaxation processes of molecules of components considered microscopically and modeled by anharmonic oscillators during collisions with molecules of components considered macroscopically and modeled by harmonic oscillators

$$\{f; v_m, v_n\} \overset{P_{ij}^{(q)}}{\rightleftharpoons} \{f - l_{iq}; v_m - l_{mq}, v_n + l_{nq}\}. \tag{1.5}$$
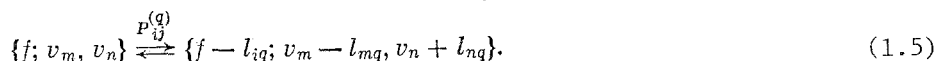
In a q-th process of such kind, a change in the quantum number f of molecules, an anharmonic oscillator of the species i, by $\pm l_{iq}$ is accompanied by a change in the quantum numbers v_m and v_n of the modes, harmonic oscillators m and n of molecules of the species j, by $\pm l_{mq}$ and $\mp l_{nq}$, respectively. By virtue of using the harmonic oscillator model for modes m and n, a process of type (1.5) is characterized by the probability

$$P_{ij}^{(q)}(f) = P \begin{Bmatrix} f, & f - l_{iq} \\ l_{mq}, & 0 \\ 0, & l_{nq} \end{Bmatrix}.$$

For a given translational gas temperature T and pressure p (or density ρ) the mixture state is determined by values of the component concentration n_i per unit mass of mixture, by the mean energies ε_k of the modes considered macroscopically, and by the relative populations of the vibrational levels of the modes considered microscopically:

$$x_{if} = n_{if}/n_i \tag{1.6}$$

(n_{if} is the concentration of the i-th component in the vibrational state f).

2. EQUATIONS FOR THE CONCENTRATIONS

Under assumptions "a" and "b" the equations for the component concentration per unit mass n_i have the form

$$\frac{dn_i}{dt} = \sum_r (v'_{ir} - v_{ir})(R_r - R'_r), \quad i = 1, 2, \ldots, N. \tag{2.1}$$

If the r-th chemical reaction refers to the type (1.1), then

$$R_r = k_r \prod_{j=1}^{N} (\rho n_j)^{v_{jr}}, \quad R'_r = k'_r \prod_{j=1}^{N} (\rho n_j)^{v'_{jr}} \tag{2.2}$$

with the rate constants $k_r(T, T_k)$ and $k'_r(T, T_k)$ dependent on the translation temperature and the vibrational temperatures T_k (the mean vibrational energies ε_k) of the modes taking part in the molecule reaction (see details in [2]).* In the general case of a polyatomic molecule, the vibrational temperature and mean energy (mean store of vibrational quanta) of the k-th mode are connected by the relationship [1]

$$\exp(-\theta_k/T_k) = \varepsilon_k/(\lambda_k + \varepsilon_k),$$

where θ_k and λ_k are the magnitude of the vibrational quantum of the transition $1 \to 0$ in degrees and the degree of degeneration of the k-th mode.

If the r-th chemical reaction is among the type (1.2), then

$$R_r = \sum_f k_r(f) x_{if}^{v_{ir}} \prod_{j=1}^{N} (\rho n_j)^{v_{jr}}, \quad R'_r = \sum_f k'_r(f) x_{if}^{v'_{ir}} \prod_{j=1}^{N} (\rho n_j)^{v'_{jr}},$$

$$k_r(f) = k_r g_r(f), \quad \sum_f g_r(f) = 1, \quad k'_r(f) = k_r(f)/[x_{if}^0 K_r(T)]. \tag{2.3}$$

Here $g_r(f)$ is the vibrational distribution of the i-th component in the r-th reaction, $x_{if}^0 = x_{if}(T)$ is the equilibrium value of x_{if}, and $K_r = K_r(T)$ is the equilibrium constant for the appropriate integral reaction.

3. EQUATIONS FOR THE MEAN ENERGIES OF MODES CONSIDERED MACROSCOPICALLY

Sequential deduction of kinetic equations for mean vibrational energies ε_k from the population balance equations under assumptions "b," "c" is executed in [1]; taking account of the influence of the chemical reactions, the equations for ε_k have the form [2]

$$\frac{d\varepsilon_k}{dt} = \sum_q l_{kq} A_q (Q_q - Q'_q) + \sum_r (v'_{jr} - v_{jr})[(\chi_{rk} - \varepsilon_k) R_r - (\chi'_{rk} - \varepsilon_k) R'_r]/\rho n_j, \tag{3.1}$$

k = 1, 2, ..., S (the mode k belongs to the molecule of species j)

$$Q_q = \prod_m \left[\frac{\varepsilon_m^0 (\lambda_m + \varepsilon_m)}{\lambda_m (\lambda_m + \varepsilon_m^0)} \right]^{l_{mq}} \prod_n \left[\frac{\varepsilon_n^0 (\lambda_n + \varepsilon_n^0)}{\lambda_n \varepsilon_n^0} \right]^{l_{nq}},$$

$$Q'_q = \prod_m \left(\frac{\varepsilon_m}{\lambda_m} \right)^{l_{mq}} \prod_n \left(\frac{\lambda_n + \varepsilon_n}{\lambda_n} \right)^{l_{nq}}, \quad A_q = \sum_{i=1}^{N} Z_{ji} P_{ji}^{(q)} \prod_m \binom{l_{mq} + \sigma_{ji} \lambda_m - 1}{l_{mq}}$$

(processes of the type (1.3) as well as processes of the type (1.5) written as integrals with respect to f, i.e., analogous to (1.3), are taken into account in the summation over q). Here S is the complete number of modes considered macroscopically, $\varepsilon_k^0 = \varepsilon_k(T)$ is the equilibrium

*The dependences of the reaction rate constants on the vibrational temperatures of the corresponding modes, presented in [2], have been obtained [4, 5] within the framework of assumptions "a"–"c" for the specific case of a dissociation reaction. However, to derive these dependences, the concretization mentioned is not the principal and they are of substantially more general nature.

value of ε_k; $\sigma_{ji} = 1 + \delta_{ji}$ (δ_{ji} is the Kronecker delta), $\chi_{rk}(\chi_{rk})$ is the mean number of vibrational quanta obtained (lost) by the k-th mode in one act of generation (annihilation) of molecules of species j in the r-th reaction (see [2] for details). Reactions of the type (1.1) as well as reactions of the type (1.2) in which the macroscopic component under consideration j written as an integral with respect to f, i.e., analogous to (1.1), takes part are taken into account in the summation over r. The mean energies of modes considered microscopically (taking account of processes of the type (1.5)) can be in the expressions for Q_q and Q_q':

$$\varepsilon_i = \sum_f f\left(1 - f/2W_i\right) x_{if}, \quad W_i = (\omega_0)_i/2\,(\omega_e x_e)_i,$$

where $(\omega_0)_i$ and $(\omega_e x_e)_i$ and the fundamental frequency and the spectroscopic constant of anharmony of the i-th vibration, and x_{if} is the relative population of the f-th vibrational state of the i-th component considered microscopically.

4. EQUATIONS FOR x_{if}

The relative populations of the vibrational states of diatomic molecules, anharmonic oscillators considered microscopically, can change because of the processes (1.2), (1.4), and (1.5), i.e.,

$$\frac{dx_{if}}{dt} = \left(\frac{dx_{if}}{dt}\right)_2 + \left(\frac{dx_{if}}{dt}\right)_4 + \left(\frac{dx_{if}}{dt}\right)_5,$$

where according to definition (1.6)

$$\sum_f x_{if} = 1. \tag{4.1}$$

Because of the progress of the detailed (microscopic) chemical reactions (1.2), the change in x_{if} satisfying the normalization condition (4.1) is

$$\left(\frac{dx_{if}}{dt}\right)_2 = \frac{1}{\rho n_i} \sum_r \left(v_{ir}' - v_{ir}\right)\left[R_r(f) - R_r'(f)\right], \tag{4.2}$$

where the quantities $R_r(f)$ and $R_r'(f)$ are determined by (2.3).

The change in x_{if} because of the progress of vibrational relaxation processes of the type (1.4) for diatomic molecule collisions, anharmonic oscillators of one (i = j) or different (i ≠ j) species, under assumption "b" has the form of the right side of the kinetic equations for a binary mixture of diatomic molecules (see [6], e.g.). Taking account of the principle of detailed equilibrium and assumption "d," we obtain in most general form

$$\left(\frac{dx_{if}}{dt}\right)_4 = \sum_q \left(x_{i,f-l_{iq}} \sum_{s=l_{jq}}^{W_j} x_{js} \exp\left[\frac{\theta_j}{T} l_{jq}\left(1 - \frac{2s - l_{jq}}{2W_j}\right) - \right.\right.$$
$$\left. - \frac{\theta_i}{T} l_{iq}\left(1 - \frac{2f - l_{iq}}{2W_i}\right)\right]\Omega_{f,f-l_{iq}}^{s-l_{jq},s} + x_{i,f+l_{iq}} \sum_{s=0}^{W_j-l_{jq}} x_{js}\Omega_{f+l_{iq},f}^{s,s+l_{jq}} - \tag{4.3}$$
$$\left. - x_{if}\left\{\sum_{s=l_{jq}}^{W_j} x_{js} \exp\left[\frac{\theta_j}{T} l_{jq}\left(1 - \frac{2s - l_{jq}}{2W_j}\right) - \frac{\theta_i}{T} l_{iq}\left(1 - \frac{2f + l_{iq}}{2W_i}\right)\right]\Omega_{f+l_{iq},f}^{s-l_{jq},s} + \sum_{s=0}^{W_j-l_{jq}} x_{js}\Omega_{f,f-l_{iq}}^{s,s+l_{jq}}\right\}\right),$$

where

$$\Omega_{f,f'}^{s,s'} = \sum_j Z_{ij} P_{f,f'}^{s,s'}; \tag{4.4}$$

Z_{ij} is the number of collisions of molecules of species i per unit time with molecules of species j for a unit concentration of molecules of the species i, and summation over j is executed in the case of VT-exchange (s = s' = 0).

The change in x_{if} because of the progress of processes of type (1.5) is written first in the form of appropriate population balance equations for the vibrational states

$$\left(\frac{dx_{if}}{dt}\right)_5 = \sum_q \sum_{\{v_m,v_n\}} \left[x_{i,f-l_{iq}}\, y\{v_m - l_{mq}, v_n + l_{nq}\}\, \Omega\begin{Bmatrix} t - l_{iq}, f \\ v_m - l_{mq}, v_m \\ v_n + l_{nq}, v_n \end{Bmatrix} - \right. \tag{4.5}$$

$$x_{if},\, y\{v_m, v_n\}\, \Omega\begin{Bmatrix} f, f - l_{iq} \\ v_m, v_m - l_{mq} \\ v_n, v_n + l_{nq} \end{Bmatrix} + x_{i,f+l_{iq}}\, y\{v_m + l_{mq}, v_n - l_{nq}\}\, \Omega\begin{Bmatrix} f + l_{iq}, f \\ v_m + l_{mq}, v_m \\ v_n - l_{nq}, v_n \end{Bmatrix} - x_{if}\, y\{v_m, v_n\}\, \Omega\begin{Bmatrix} f, f + l_{iq} \\ v_m, v_m + l_{mq} \\ v_n, v_n - l_{nq} \end{Bmatrix}\Bigg]$$

where

$$\Omega \begin{Bmatrix} f, f' \\ v_m, v'_m \\ v_n, v'_n \end{Bmatrix} = Z_{ij} P \begin{Bmatrix} f, f' \\ v_m, v'_m \\ v_n, v'_n \end{Bmatrix}; \tag{4.6}$$

$y\{v_s\} = n_j\{v_s\}/n_j$ is the relative population of the vibrational state $\{v_s\} = (v_1, v_2, \ldots, v_{b_j})$ of a polyatomic molecule of the species j. Taking account of the detailed equilibrium principle and the expressions for the populations of the vibrational states of molecules of species j resulting from assumption "c"

$$y\{v_s\} = \prod_{s=1}^{b_j} \frac{(v_s + \lambda_s - 1)!}{v_s! (\lambda_s - 1)!} \frac{\lambda_s^{\lambda_s} \varepsilon_s^{v_s}}{(\lambda_s + \varepsilon_s)^{\lambda_s + v_s}} \tag{4.7}$$

in the case of diatomic molecules, Morse oscillators, we have

$$(4.8) \quad \left(\frac{dx_{if}}{dt}\right)_5 = \sum_q \left\{ \left[x_{i,f-l_{iq}} e^{-\frac{\theta_i}{T} l_{iq}\left(1 - \frac{2f - l_{iq}}{2W_i}\right)} B_q - x_{if} \right] C_q(f, f - l_{iq}) - \left[x_{if} e^{-\frac{\theta_i}{T} l_{iq}\left(1 - \frac{2f + l_{iq}}{2W_i}\right)} B_q - x_{i,f+l_{iq}} \right] C_q(f + l_{iq}, f) \right\}_i \tag{4.8}$$

where

$$B_q = \prod_m \left[\frac{\varepsilon_m^0 (\lambda_m + \varepsilon_m)}{\varepsilon_m (\lambda_m + \varepsilon_m^0)} \right]^{l_{mq}} \prod_n \left[\frac{\varepsilon_n (\lambda_n + \varepsilon_n^0)}{\varepsilon_n^0 (\lambda_n + \varepsilon_n)} \right]^{l_{nq}}; \tag{4.9}$$

$$C_q(f, f') = \sum_{\{v_m, v_n\}} y\{v_m, v_n\} \Omega \begin{Bmatrix} f, f' \\ v_m, v_m - l_{mq} \\ v_n, v_n + l_{nq} \end{Bmatrix}. \tag{4.10}$$

Further manipulation of (4.8)-(4.10) consists of simplifying (4.10) and is associated with utilization of the relationship

$$P \begin{Bmatrix} f, f' \\ v_m, v_m - l_{mq} \\ v_n, v_n + l_{nq} \end{Bmatrix} = P \begin{Bmatrix} f, f' \\ l_{mq}, 0 \\ 0, l_{nq} \end{Bmatrix} \prod_m \frac{v_m!}{l_{mq}! (v_m - l_{mq})!} \prod_n \frac{(v_n + l_{nq} + \lambda_n - 1)! (\lambda_n - 1)!}{(v_n + \lambda_n - 1)! (l_{nq} + \lambda_n - 1)!}, \tag{4.11}$$

analogous to that obtained in [1] for the probability of the process (1.3). Taking account of (4.6), (4.7), and (4.11), it can be shown that

$$C_q(f, f') = \Omega \begin{Bmatrix} f, f' \\ l_{mq}, 0 \\ 0, l_{nq} \end{Bmatrix} \prod_m \frac{\lambda_m^{\lambda_m} \varepsilon_m^{l_{mq}}}{(\lambda_m - 1)! \, l_{mq}! \, (\lambda_m + \varepsilon_m)^{\lambda_m + l_{mq}}} \times$$

$$\times \sum_{w_m=0}^{\infty} \frac{(w_m + l_{mq} + \lambda_m - 1)!}{w_m!} \left(\frac{\varepsilon_m}{\lambda_m + \varepsilon_m} \right)^{w_m} \prod_n \frac{[\lambda_n/(\lambda_n + \varepsilon_n)]^{\lambda_n}}{(l_{nq} + \lambda_n - 1)!} \sum_{v_n=0}^{\infty} \frac{(v_n + l_{nq} + \lambda_n - 1)!}{v_n!} \left(\frac{\varepsilon_n}{\lambda_n + \varepsilon_n} \right)^{v_n}.$$

Summing over w_m and v_n

$$\sum_{k=0}^{\infty} \frac{(k+n)!}{k!} x^k = \frac{n!}{(1-x)^{n+1}}, \quad x < 1,$$

we obtain

$$C_q(f, f') = \Omega \begin{Bmatrix} f, f' \\ l_{mq}, 0 \\ 0, l_{nq} \end{Bmatrix} \prod_m \binom{l_{mq} + \lambda_m - 1}{l_{mq}} \left(\frac{\varepsilon_m}{\lambda_m} \right)^{l_{mq}} \prod_n \left(\frac{\lambda_n + \varepsilon_n}{\lambda_n} \right)^{l_{nq}}. \tag{4.12}$$

Thus, we finally have as the equations for the relative populations of the vibrational states of diatomic molecules, Morse oscillators, considered microscopically:

$$\frac{dx_{ij}}{dt} = \frac{1}{\rho n_i} \sum_r (v'_{ir} - v_{ir})\left[R_r(f) - R'_r(f)\right] +$$

$$+ \sum_q \left(x_{i,f-l_{iq}} \sum_{s=l_{jq}}^{W_j} x_{js} \exp\left[\frac{\theta_j}{T} l_{jq}\left(1 - \frac{2s - l_{jq}}{2W_j}\right) - \frac{\theta_i}{T} l_{iq}\left(1 - \frac{2f - l_{iq}}{2W_i}\right)\right] \times \right.$$

$$\times \Omega_{f,f-l_{iq}}^{s-l_{jq},s} + x_{i,f+l_{iq}} \sum_{s=0}^{W_j-l_{jq}} x_{js}\Omega_{f+l_{iq},f}^{s,s+l_{jq}} - x_{if}\left\{\sum_{s=l_{jq}}^{W_i} x_{js} \exp\left[\frac{\theta_j}{T} l_{jq}\left(1 - \frac{2s - l_{jq}}{2W_j}\right) - \right.\right. \tag{4.13}$$

$$\left. - \frac{\theta_i}{T} l_{iq}\left(1 - \frac{2f + l_{iq}}{2W_i}\right)\right]\Omega_{f+l_{iq},f}^{s-l_{jq},s} + \sum_{s=0}^{W_j-l_{jq}} x_{js}\Omega_{f,f-l_{iq}}^{s,s+l_{jq}}\right\} +$$

$$+ \sum_q \left\{\left[x_{i,f-l_{iq}}e^{-\frac{\theta_i}{T} l_{iq}\left(1 - \frac{2f - l_{iq}}{2W_i}\right)}B_q - x_{if}\right]C_q(f, f - l_{iq}) - \left[x_{if}e^{-\frac{\theta_i}{T} l_{iq}\left(1 - \frac{2f + l_{iq}}{2W_i}\right)}B_q - x_{i,f+l_{iq}}\right]C_q(f + l_{iq}, f)\right\},$$

where the quantities $R_r(f)$, $R'_r(f)$, $\Omega_{f,f'}^{s,s'}$, B_q, and $C_q(f, f')$ are determined, respectively, by the relations (2.3), (4.4), (4.9), and (4.12), (4.6). Only chemical reactions of the type (1.2) are taken into account in (4.13) in the summation over r, while only processes of the type (1.4) are taken into account in the summation over q in the first sum and only processes of the type (1.5) in the second sum.

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INFLUENCE OF NONEQUILIBRIUM OF THE CHEMICAL COMPOSITION OF A GAS ON ITS MOTION

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We consider a gas cloud in which chemical equilibrium is disturbed, which can be accomplished, for example, by a pulse of ionizing or dissociating radiation. In this case the specific thermal energy e_t can be far lower than the specific chemical energy e_c, i.e., the energy expended on breaking chemical bonds, the excitation of levels, and ionization.

In the process of relaxation of the nonequilibrium state of the gas the chemical energy is converted into thermal energy and the initially stationary gas starts to expand. The decrease in density during the dispersal causes a decrease in the rates of the chemical reactions, and the transfer of chemical into thermal energy is slowed, which in turn influences the intensity of dispersal. In such phenomena the gasdynamic processes and processes of chemical kinetics are closely connected with each other. A joint solution of the equations of gasdynamics (GD) and chemical kinetics (CK) is required for their correct description. Here the solution even of the CK equations alone causes considerable difficulties, since the corresponding system is "strict" [1]. Sufficiently effective methods of solving such systems were recently developed [2, 3]. However, for a moving gas additional difficulties