Non-equilibrium reaction rates and non-equilibrium effects in chemical kinetics

Yu E Gorbachev
Coddan Technologies LLC, Belooostrovskaya str., 22, St.-Petersburg, 197342 Russia
E-mail: yuriy.gorbachev@gmail.com

Abstract. Non-equilibrium effects of different nature and their impact on the reaction and relaxation rates of the reacting gas mixture are considered. Expression for the dissociation rate is obtained employing the asymptotic method of solving Boltzmann equation, developed in the previous papers (Kolesnichenko, Gorbachev, 2010, 2013, Gorbachev 2016). Application of the projection method for solving the integral equations for zeroth-order corrections to quasi-equilibrium distributions is examined. Possibilities of simplifying of the expressions for reaction rates are discussed.

1. Introduction
High-enthalpy chemically reactive flows are of great interest both for theoretical research and technical applications. Chemical kinetic equations used for simulating such flows are either phenomenological with the equilibrium reaction rates calculated via Guldberg and Waage law or obtained within the generalized Chapman-Enskog method under Prigogine’s assumption [1]. The last reads as: in the corresponding Boltzmann equation the part of the collisional integral, responsible for the chemical reactions, is small (of the order of Knudsen number) in comparison with the non-reactive part. Most of such calculations are performed employing the equilibrium reaction rates [2-4]. Only several studies employ the non-equilibrium reaction rates for dissociation processes (thermal dissociation) [5-7]. Equations for the rates of these reactions (being the type of the unimolecular reactions [8]) are discussed in details in [9]. Quasi-stationary state (QSS) method for reaction rate calculation is used in [5,9]. It leads to their non-trivial dependence on the species densities, that differs from the Guldberg and Waage (mass action) law, which implies that the rate $R_r$ of the reaction $r$ can be represented as $R_r = K^e_r \eta_r$, $\eta_r = \prod_\beta \eta_\beta^{v_\beta^u} - K^e_r \prod_\beta \eta_\beta^{v_\beta^d}$, where $v^{(f)}_\beta$ are corresponding stoichiometrical coefficients in the initial(final) state, the products are over all colliding partners in the initial/final channel of corresponding reaction and the equilibrium rate constants $K^e_r$ and equilibrium constant $K^e_r$ are functions of the temperature only. As discussed in [10], QSS methodology cannot be considered as a mathematically rigorous. It does not permit building the asymptotic approach for the gas-dynamic equations derivation. Only the path to calculate the quasi-stationary state (zero-order approximation) and first-order corrections are realized. Therefore, the consequential asymptotic procedure for gas-dynamic equation derivation is required. It was proposed in [11] and is based on three main points: (1) collisional integral $I$ is not expanded into the series over Knudsen number (Prigogine’s assumption is discarded); (2) the slow variables are introduced on the basis of the concept of the approximate collisional invariants and distribution function is represented as a sum of the slow
part, for which the quasi-equilibrium function is chosen, depending on time and coordinates only via gas-dynamic variables, \( \{ \Gamma \} \), and the fast part, which depends on time and coordinates explicitly: \( F = F^{\text{qe}}(\Gamma) \) + \( \Phi(t, r) \); (3) equations for those slow and fast parts are represented as a singularly perturbed set of the equations, which are solved via the modified Chapman-Enskog procedure. Within this method it was shown that not only dissociation rates, but all other are non-trivial functions of the species densities. At the same time the spatially homogeneous part of the non-equilibrium reaction rates vanishes at \( \eta_r = 0 \), while spatially inhomogeneous (proportional to the gas-dynamic velocity divergency) does not [12].

In the next section the non-equilibrium effects causing the deviation of the reaction rates in the reactive gas flows from the equilibrium are discussed, integral equations that determine the deviation functions and methods of their solving are considered, an example of the dissociation of diatomic molecules is examined and the corresponding reaction rate is derived. Final conclusions are presented in the last section.

2. Non-equilibrium reaction rates

2.1. General equations

Asymptotic method of solving the Boltzmann equation [11] leads to the following set of chemical kinetic and relaxation equations:

\[
\frac{\partial n_\alpha}{\partial t} + \nabla \cdot (u_n \alpha) = R_{\alpha}(\Gamma) = \langle \psi_n, l(F^{\text{qe}}) \rangle + \langle \psi_{n*, l'}, l'(F^{\text{qe}}) \rangle (\phi^h + \phi^d \nabla \cdot u)
\]

\[
\equiv R^{\text{qe}}_{\alpha} + R^{\text{ne}}_{\alpha} h + R^{\text{ne}}_{\alpha} d \cdot u \equiv R_{\alpha}^h + R_{\alpha}^d, \quad \Gamma = \{ \Gamma_q \}, \quad F_{\alpha} = F^{\text{qe}}_{\alpha} + \phi_{\alpha}, \quad \phi_{\alpha} = \phi_{\alpha}^h + \phi_{\alpha}^d \nabla \cdot u,
\]

\[
\frac{\partial R_{\alpha}}{\partial t} + \nabla \cdot (u R_{\alpha}) = R_{\alpha}(\Gamma) = \langle \psi_{R_{\alpha}}, l(F^{\text{qe}}) \rangle + \langle \psi_{n*, l'}, l'(F^{\text{qe}}) \rangle (\phi^h + \phi^d \nabla \cdot u)
\]

\[
\equiv R^{\text{qe}}_{\alpha} + R^{\text{ne}}_{\alpha} h + R^{\text{ne}}_{\alpha} d \cdot u \equiv R_{\alpha}^h + R_{\alpha}^d, \quad \alpha = 1, \ldots, N; \quad I \text{ is the collisional operator and } l^i \text{ is its linearized form}; \quad \Gamma_q = \langle \psi_{r_q}, F_q \rangle, \quad q = 1, \ldots, M (> N + M_a) \text{ is the whole set of gas-dynamic variables, } N + M_a \text{ is the number of approximate summational invariants (ASI)} [10,11]; \quad \langle \psi, \phi \rangle = \sum_{\alpha} \sum_{k_a} \int d \vec{v}_\alpha \psi_\alpha(\vec{v}_\alpha, k_a) \phi_\alpha(\vec{v}_\alpha, k_a) \text{ is a scalar product, } \psi_\alpha, k_a \text{ being the velocities and quantum numbers, respectively}; \quad \psi_{n_\alpha}(\beta) = \delta_{\alpha \beta} \text{ and } \psi_{r_{\alpha,j}} \text{ are non-exact ASIs, which correspond to number densities and ‘additional’ gas-dynamic variables (such as mean quantum numbers, internal temperature, etc), respectively}; \quad R^{\text{qe}}_{\alpha} \text{ and } \phi_{\alpha} \text{ are the quasi-equilibrium distributions and corresponding zeroth-order corrections, respectively}; \quad u \text{ is the mixture gas-dynamic velocity. Relaxation characteristics, i.e. reaction rates } R_{\alpha} \text{ and relaxation rates } R_{\alpha j}, \text{ have the similar structure [11], thus, } N + M_a \text{ components of vector } R \text{ are called generalized relaxation rates (GRR); } R^{h(i)} \text{ are spatially homogeneous (inhomogeneous) parts of the GRRs (under spatially homogeneous conditions, when } \partial / \partial r = 0 \text{, the term } R^i \text{ vanishes).}

As shown in our previous papers [13,14], the GRRs derived within the Euler approximation can be represented in the renormalized form

\[
R = R^{\text{qe}} + R^{\text{ne}} = R^h + R^d = (1 - A)^{-1} R^0,
\]

\[
R^0 = R^{0h} + R^{0d}, \quad R^{0i} = R^{0d} \cdot u, \quad R^{d^0} = \sum_{r \in r_a} (v^\prime_a - v^\prime_a) R^0_{r},
\]

(2)

where \( R^0 \) and \( R \) are column-matrixes with \( N + M_a \) elements of the reduced, \( \{ R^0_{q} \} = \{ R_{\alpha}, R_{\alpha j} \} \), and non-equilibrium, \( \{ R_{\alpha} \} = \{ R_{\alpha}, R_{\alpha j} \} \), GRRs, respectively; \( R^{\text{qe}} \) and \( R^{\text{ne}} \) are quasi-equilibrium reaction rates and non-equilibrium corrections, respectively; \( R^{0h} = R^{\text{qe}} + R^{\text{ne}} h \) and \( R^{0i} \)
are corresponding spatially homogeneous and spatially inhomogeneous parts; $A$ is the renormalizing (adiabatic) $(N + M_a) \times (N + M_a)$ matrix $\{A_{ij}\}$; $v_{\alpha r}^{(i)}$ are the stoichiometric coefficients of species $\alpha$ in the initial (final) channel of the reaction $r$; $R_{\alpha}^0$ are the individual reduced reaction rates; $r_\alpha$ is the set of reactions in which species $\alpha$ participates. Those reaction rates are determined by the corresponding parts of $\Phi_\alpha$:

$$
\Phi_\alpha = \Phi_\alpha^0 + \Phi_\alpha^i, \quad \Phi_\alpha^0 = \Phi_\alpha^0 \Phi \cdot u, \quad \Phi_\alpha^i = \Phi_\alpha^i \Phi \cdot u,
$$

$$
\Phi_\alpha^{0d} = \Phi_\alpha^{0d} \Phi \cdot u, \quad \Phi_\alpha^{d} = \Phi_\alpha^{0d} + \Phi_\alpha^{0d} \phi_{ax} R_{ax}^0, \quad \Phi_\alpha^{d} = \Phi_\alpha^{0h} + \Phi_\alpha^{0i}.
$$

(3)

Functions $\Phi_\alpha$ should satisfy the orthogonality conditions

$$
\langle \psi_{r_\alpha} | \Phi_\alpha \rangle = 0,
$$

(4)

thus, each of its part should also satisfy such condition. For their each part the integral equations were derived in [13,14]. Further, only one-temperature mode will be considered, for which those equations read as

$$
[l^i(F^{q})\Phi^{0h}]_\alpha = -l_\alpha(F^{q}), \quad [l^i(F^{q})\Phi_\beta^0]_\alpha = F^{q} \phi_{\alpha}^0 \left( \frac{\delta_\alpha}{{n_\alpha}} - \frac{\tilde{e}_\alpha - \tilde{e}_\alpha^E_{\alpha}}{k_B T} c_\alpha n T \right),
$$

$$
[l^i(F^{q})\Phi^{0d}_\alpha]_\alpha = \frac{\phi_{\alpha}^{q \alpha}}{c_\alpha^{\alpha}} \left( c_\alpha \left( e_\alpha^{\alpha} - \tilde{e}_\alpha^E_{\alpha} \right) - \left( e_\alpha^{\alpha} - \tilde{e}_\alpha^E_{\alpha} \right) \right),
$$

(5)

where $n = \sum_\alpha n_\alpha$; $c_\alpha^T$ and $c_\alpha^E$ are the mixture heat capacities of the translational and internal degrees of freedom, respectively, $c_\alpha = c_\alpha^T + c_\alpha^E$; $e_\alpha^i$ and $e_\alpha^l$ are translational and internal energies of species $\alpha$, $e_\alpha^E = m_\alpha c_\alpha^E/2$, $c_\alpha = v_\alpha - u$, $e_\alpha = e_\alpha^T + e_\alpha$; $T$ is the mixture temperature; $\tilde{e}_\alpha^{E(i)} = (\delta_\alpha e_\alpha^{T (i)}, F^{q})$.  

Here and further the dot in the formula $\Phi_{\alpha q}^a$ and similar means the dummy index. The RHSs of the equations for $\Phi^{0h}$ and $\Phi^a$ are the functions of the total energy $\tilde{e}_\alpha$, while the RHS of the equation for $\Phi^{0d}$ is a function of the translational and internal energies separately. Therefore, corresponding parts of the distribution functions $\Phi_{ax}^{a}(d)$ are $\Phi_{ax}^{0h(d)} / F^{q}$, $\phi_{ax}^{a} = \phi_{ax}^{a} / F^{q}$, can be sought in the form:

$$
\phi_{ax}^{a0} = \sum_{n=0} a_{a0}^{(n)} P_n \left( \gamma_E (\tilde{e}_\alpha^{E} - \tilde{e}_\alpha^{E}) \right), \quad \phi_{ax}^{0h} = \sum_{n=0} a_{a0}^{(h(n))} P_n \left( \gamma_E (\tilde{e}_\alpha^{E} - \tilde{e}_\alpha^{E}) \right),
$$

$$
\phi_{ax}^{a} = \sum_{m=0} a_{ax}^{(d(n,m))} P_m \left( \gamma_E (\tilde{e}_\alpha^{E} - \tilde{e}_\alpha^{E}) \right), \quad \psi_{r_\alpha} = \psi_{r_\alpha} = \delta_\alpha \beta, \quad \gamma_E = 1/k_B T,
$$

(6)

where $P_n$ are the orthogonal polynomials of the order $n$. Due to the orthogonality conditions (4) calculated with $\psi_{r_\alpha} = \psi_{r_\alpha} = \delta_\alpha \beta$, all zeroth order coefficients vanish: $a_{a0}^{(0)} = a_{a0}^{(h(0))} = a_{ax}^{(d(0,0))} = 0$.

For deriving the equations for the $a$-coefficients from the equations (5), after substituting the equations (6), the obtained equations should be projected onto the suitable complete set of functions. In so doing, the features of the collisional integrals in the LHS's of those equations, namely the existence of the collisional invariants should be taken into account. If the aforementioned equations are obtained by projecting the equations (5) only on the functions that are not the collisional invariants, the nongenerated set of equations is obtained, therefore the orthogonal conditions (4) cannot be satisfied. Since the energy $\tilde{e}_\alpha$ is a collisional invariant, while constants, $\tilde{e}_\alpha^{E}$, for instance, are not, the projection on $\delta_\alpha \beta \tilde{e}_\alpha$ should be calculated for the corresponding equations derivation. The sum of the obtained equations is an identity, therefore the corresponding set of equations is degenerate. Considering only first non-zeroth terms in the expansions (6), the following relationships can be derived:
\[
\Sigma r \epsilon a \left( \Sigma Y e \nu ^{r} \gamma b \nu ^{a} \delta \left[ v_{\nu} e_{a}^{r} - v_{\nu} e_{a}^{r}, e_{a}^{r}, \tilde{g}_{a}^{r} - \tilde{g}_{a}^{r}, e_{a}^{r} - \tilde{g}_{a}^{r} \right] \right) = \delta^{a}_{a} - \frac{\gamma e a}{c_{a}} \left[ \delta^{a}_{a} - \frac{\gamma e a}{c_{a}} \right] = a_{\gamma b}^{a}(1) = a_{\gamma b}^{a}(1) \gamma e \tilde{g} \beta e_{\beta},
\]

(7)

\[
\Sigma r \epsilon a \left( \Sigma Y e \nu ^{r} \gamma b \nu ^{a} \delta \left[ v_{\nu} e_{a}^{r} - v_{\nu} e_{a}^{r}, e_{a}^{r}, \tilde{g}_{a}^{r} - \tilde{g}_{a}^{r}, e_{a}^{r} - \tilde{g}_{a}^{r} \right] \right) = \delta^{a}_{a} - \frac{\gamma e a}{c_{a}} \left[ \delta^{a}_{a} - \frac{\gamma e a}{c_{a}} \right] = a_{\gamma b}^{a}(1) = a_{\gamma b}^{a}(1) \gamma e \tilde{g} \beta e_{\beta},
\]

(8)

\[
\Sigma r \epsilon a \left( \Sigma Y e \nu ^{r} \gamma b \nu ^{a} \delta \left[ v_{\nu} e_{a}^{r} - v_{\nu} e_{a}^{r}, e_{a}^{r}, \tilde{g}_{a}^{r} - \tilde{g}_{a}^{r}, e_{a}^{r} - \tilde{g}_{a}^{r} \right] \right) = \delta^{a}_{a} - \frac{\gamma e a}{c_{a}} \left[ \delta^{a}_{a} - \frac{\gamma e a}{c_{a}} \right] = a_{\gamma b}^{a}(1) = a_{\gamma b}^{a}(1) \gamma e \tilde{g} \beta e_{\beta},
\]

(9)

\[
\Sigma r \epsilon a \left( \Sigma Y e \nu ^{r} \gamma b \nu ^{a} \delta \left[ v_{\nu} e_{a}^{r} - v_{\nu} e_{a}^{r}, e_{a}^{r}, \tilde{g}_{a}^{r} - \tilde{g}_{a}^{r}, e_{a}^{r} - \tilde{g}_{a}^{r} \right] \right) = \delta^{a}_{a} - \frac{\gamma e a}{c_{a}} \left[ \delta^{a}_{a} - \frac{\gamma e a}{c_{a}} \right] = a_{\gamma b}^{a}(1) = a_{\gamma b}^{a}(1) \gamma e \tilde{g} \beta e_{\beta},
\]

(10)

Here \( \Delta v_{\nu} \), \( v_{\nu} \), and \( e_{\gamma} \) are bracket integrals for reactive collisions, which correspond to reaction \( r \) characterized by the initial \( \nu^{r} \) and final \( \nu^{r} \) sets of species:

\[
\left[ e_{\gamma}, e_{\gamma} - e_{\gamma} \right] = \gamma^{2} \sum_{k_{\nu}^{r} k_{\gamma}^{r}} d v_{\nu}^{r} d v_{\gamma}^{r} e_{\gamma}^{r} W_{\gamma}^{r} e_{\gamma}^{r} \frac{e_{\gamma}^{r} e_{\gamma}^{r}}{P_{\gamma}^{r} Q_{\gamma}^{r}} = c_{\gamma}^{r} e_{\gamma}^{r},
\]

where \( W_{\gamma}^{r} \) is the probability of reactive collisions that satisfies the microscopic reversibility law and contains \( \delta \)-functions of momentum and energy conservation laws; \( Q_{\gamma} \) are partition functions; \( e_{\gamma}^{r} = \sum_{k_{\nu}^{r} k_{\gamma}^{r}} e_{\gamma}^{r} \). Equations (9) and (10) are obtained by projecting equation (5) for \( \Phi^{0d} \) onto \( e_{\gamma}^{r} \) and \( e_{\gamma}^{r} \), respectively. \( [e_{\gamma}, e_{\gamma}]_{k_{\nu}^{r} k_{\gamma}^{r}} \) are bracket integrals for non-reactive collisions:

\[
\left[ e_{\gamma}, e_{\gamma} \right] = \gamma^{2} \sum_{k_{\nu}^{r} k_{\gamma}^{r}} d v_{\nu}^{r} d v_{\gamma}^{r} e_{\gamma}^{r} W_{\gamma}^{r} e_{\gamma}^{r} \frac{e_{\gamma}^{r} e_{\gamma}^{r}}{2Q_{\gamma}} = c_{\gamma}^{r} e_{\gamma}^{r},
\]

where \( \beta = a, \delta \); subindex \( a, \delta \) denotes the colliding partners; \( W_{a, \delta}^{a, \delta} \) is the probability of non-reactive collisions. Energy transfer coefficient are defined as

\[
\beta_{\nu}^{r}(1) = a_{\nu}^{r}(1), \quad a_{\nu}^{r}(1) = \sum_{k_{\nu}, k_{\gamma}} d v_{\nu}^{r} d v_{\gamma}^{r} W_{a, \delta}^{a, \delta} \frac{e_{\gamma}^{r} e_{\gamma}^{r}}{2Q_{\gamma}} \frac{e_{\gamma}^{r} e_{\gamma}^{r}}{P_{\gamma}^{r} Q_{\gamma}^{r}} e_{\gamma}^{r},
\]

(11)

Due to the degeneracy, equations (7)-(10) for \( a \)-coefficients should be complemented by the orthogonality conditions

\[
\Sigma_{a} \tilde{g} a \delta^{a} a \beta = 0, \quad \Sigma_{a} \tilde{g} a \delta^{a} a \beta h^{a} = 0, \quad \Sigma_{a} \left( \tilde{g} a \delta^{a} a \beta + \tilde{g} a \delta^{a} a \beta h^{a} \right) n_{a} = 0.
\]

Equations (7)-(10) differ from the corresponding equations in [15] by the terms in their LHSs, containing bracket integrals responsible for the reactive collisions. Equation (7) also differs by the
term $\delta_{\alpha\beta}$ in its RHS. The last term leads to non-separable expressions for the $a_{\alpha\beta}^{(1)}$ coefficients, that complicates calculation of the resolvent $(1 - A)^{-1}$.

Different parts of the reaction rates expressed via $\alpha$-coefficients read as

$$A_{\alpha\beta} = A_{\alpha\beta} y E_{\beta} R_{\beta}, \quad A_{\alpha\beta} = \gamma E \sum_{r \in r_{\alpha}} \Delta v_{\alpha} K_{r}^{\alpha} \left( \eta_{\alpha}^{r} \sum_{r \in r_{\alpha}} a_{\alpha\beta}^{(1)} \epsilon_{E_{\beta}}^{r} \beta_{E_{\beta}}^{r} - K_{r}^{\alpha} \eta_{\beta}^{r} \sum_{r \in r_{\beta}} a_{\alpha\beta}^{(1)} \epsilon_{E_{\beta}}^{r} \beta_{E_{\beta}}^{r} \right),$$

$$R_{\alpha}^{0} = R_{\alpha}^{\alpha} + \gamma E \sum_{r \in r_{\alpha}} \Delta v_{\alpha} K_{r}^{\alpha} \left( \eta_{\alpha}^{r} \sum_{r \in r_{\alpha}} a_{\alpha\beta}^{(1)} \epsilon_{E_{\beta}}^{r} \beta_{E_{\beta}}^{r} - K_{r}^{\alpha} \eta_{\beta}^{r} \sum_{r \in r_{\beta}} a_{\alpha\beta}^{(1)} \epsilon_{E_{\beta}}^{r} \beta_{E_{\beta}}^{r} \right),$$

$$R_{\alpha}^{\alpha} = \gamma E \sum_{r \in r_{\alpha}} \Delta v_{\alpha} K_{r}^{\alpha} \left( \eta_{\alpha}^{r} \sum_{r \in r_{\alpha}} a_{\alpha\beta}^{(1)} \epsilon_{E_{\beta}}^{r} \beta_{E_{\beta}}^{r} + a_{\alpha}^{d(1)} \epsilon_{E_{\beta}}^{r} \beta_{E_{\beta}}^{r} \right),$$

As a result, the non-equilibrium reaction rates can be expressed as

$$R_{\alpha} = \sum_{r \in r_{\alpha}} F_{r} R_{r}, \quad R_{r} = \gamma E \sum_{r \in r_{\alpha}} \Delta v_{\alpha} \left( \eta_{\alpha}^{r} + k_{r}^{h(r)} \eta_{\alpha}^{r} - K_{r}^{\alpha} \eta_{\beta}^{r} \sum_{r \in r_{\beta}} a_{\alpha\beta}^{(1)} \epsilon_{E_{\beta}}^{r} \beta_{E_{\beta}}^{r} \right) \nabla \cdot \mathbf{u},$$

$$k_{r}^{h(r)} = \gamma E \sum_{r \in r_{\alpha}} \Delta v_{\alpha} \left( \eta_{\alpha}^{r} \sum_{r \in r_{\alpha}} a_{\alpha\beta}^{(1)} \epsilon_{E_{\beta}}^{r} \beta_{E_{\beta}}^{r} + a_{\alpha}^{d(1)} \epsilon_{E_{\beta}}^{r} \beta_{E_{\beta}}^{r} \right).$$

### 2.2. Homonuclear diatomic molecules dissociation

For the diatomic gas dissociation two following reactions should be considered: 1. $A_{2} + A_{2} \leftrightarrow A_{2} + 2A$, 2. $A_{2} + A \leftrightarrow 3A$, so that $\nu_{A_{2}}^{2} = 1, \nu_{A_{2}}^{2} = 1, \nu_{A_{2}}^{0} = 0, \nu_{A_{1}}^{0} = 0, \nu_{A_{2}}^{2} = 1, \nu_{A_{2}}^{3} = 3; \eta_{1}^{2} = n_{2}^{2} A_{2}, \eta_{1}^{2} = n_{2}^{2} n_{2}, \eta_{2}^{2} = n_{2}^{2} \eta_{2}^{2}$. Since $A_{\alpha\beta} = -2A_{\alpha\beta}$ and $c_{\alpha\beta} a_{\alpha\beta} / \epsilon_{r_{\beta}} = -c_{\alpha\beta} a_{\alpha\beta} / \epsilon_{r_{\beta}}$, the calculated resolvent matrix elements can be expressed as $(I - A)^{-1} A_{2} = (1 + 2A_{2} - A_{2} A_{2}) / (1 + 2A_{2} - A_{2} A_{2})$. Therefore, the homogeneous part of the reaction rate, $R_{A_{2}}^{0}$, reads as

$$R_{A_{2}}^{0} = \frac{k_{1}^{c} \left[ 1 + k_{r}(1 + 2 \beta_{A_{2}} - \beta_{A_{2} A_{2}}) \right] n_{2}^{2} A_{2} + k_{2}^{c} \left[ 1 + k_{r}(1 + \beta_{A_{2} A_{2}}) \right] n_{2}^{2} A_{2} / (1 + c_{\alpha\beta} a_{\alpha\beta} / \epsilon_{r_{\beta}})}{1 + k_{r}^{c} \left[ 2c_{\alpha\beta} A_{2} n_{2}^{2} / \epsilon_{r_{\beta}} + 2c_{\alpha\beta} a_{\alpha\beta} / \epsilon_{r_{\beta}} \right]},$$

$$K_{c}^{1} = K_{c}^{2} \equiv K_{c}, \quad k_{r} = \frac{\gamma E \epsilon_{r_{2}}^{A_{2}}}{2 \epsilon_{r_{2}}^{A_{2}} A_{2} / \epsilon_{r_{2}}^{A_{2}} A_{2} + 2c_{\alpha\beta} a_{\alpha\beta} / \epsilon_{r_{2}}^{A_{2}} A_{2}},$$

$$\tau^{-1} = -K_{c}^{1} \left[ 2 \beta_{A_{2}} n_{2} - K_{c}^{1} n_{2} \left( 2 \beta_{A_{2}} n_{2} - \beta_{A_{2} A_{2}} n_{2} \right) \right] - K_{c}^{2} \left( \beta_{A_{2}} n_{2} - \beta_{A_{2} A_{2}} n_{2} + 3 \beta_{A_{2} A_{2}} n_{2} \right),$$

$$\tau_{A_{2} A_{2}}^{-1} = n \left[ \epsilon_{r_{2}}^{A_{2}} \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} n_{2} + \epsilon_{r_{2}}^{A_{2}} \left( 4 \left[ \epsilon_{r_{2}}^{A_{2}} \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} - \epsilon_{r_{2}}^{A_{2}} \epsilon_{r_{2}}^{A_{2}} \right] x_{A_{2}} - \left[ \epsilon_{r_{2}}^{A_{2}} \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} - \epsilon_{r_{2}}^{A_{2}} \epsilon_{r_{2}}^{A_{2}} \right] K_{c}^{1} x_{A_{2}} n_{A_{2}} \right) + \left[ 3 \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} - \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} - \epsilon_{r_{2}}^{A_{2}} \epsilon_{r_{2}}^{A_{2}} \right] a_{A_{2}} n_{A_{2}} - 3 \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} + \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} \right) x_{A_{2}},$$

$$\tau_{A_{2} A_{2}}^{-1} = n \left[ \epsilon_{r_{2}}^{A_{2}} \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} n_{2} + \epsilon_{r_{2}}^{A_{2}} \left( 4 \left[ \epsilon_{r_{2}}^{A_{2}} \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} - \epsilon_{r_{2}}^{A_{2}} \epsilon_{r_{2}}^{A_{2}} \right] K_{c}^{1} x_{A_{2}} x_{A_{2}} - 3 \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} + \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} \right) x_{A_{2}},$$

$$[\epsilon_{r_{2}}^{A_{2}} a_{A_{2}} - \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} - \epsilon_{r_{2}}^{A_{2}} \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} + \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} \right] x_{A_{2}} + \epsilon_{r_{2}}^{A_{2}} \left( 3 \left[ \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} - \epsilon_{r_{2}}^{A_{2}} \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} - \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} + \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} \epsilon_{r_{2}}^{A_{2}} a_{A_{2}} \right) x_{A_{2}} \right).$$
where $x_a = n_a/n$. For other rates we have $R_{A}^h = -2R_{A}^A$ and $R_A = -2R_A$. Spatially inhomogeneous part has a more complex form, therefore it will be presented elsewhere. Neglecting the terms in the equations for $\tau_{A_2A_2}^{-1}$ and $\tau_{A_2A}^{-1}$ responsible for reactions, simplifies corresponding expressions

$$\tau_{A_2A_2}^{nr-1} = \tau_{A_2A}^{nr-1} = n[\tilde{a}_{A_2A_2}]_{AA_2}^{nr} \equiv \tau_{A_2}^{nr-1}.$$  \hspace{1cm} (18)

Another simplification can be done when approximation $\tilde{r}_a = c_{eq}T$ is applied.

3. Conclusion

Obtained equation for the dissociation rate contains sums of the bracket integrals. Those sums in (17) as well as in the initial equations for $a$-coefficients (7)-(10), consist of the reactive and non-reactive terms. As shown in [16], for getting the uniform asymptotic solution of the Boltzmann equation the reactive part of the collisional integral shouldn’t be considered as a small perturbation. Equations (7)-(10) are the finite approximations of corresponding integral equations, therefore, in general, both reactive and non-reactive bracket integrals should be considered while corresponding reaction rates calculations. Still, for simplifying and estimating those rates and analysing their non-trivial dependence on species densities, only non-reactive bracket integrals can be considered. This leads to the equations (18).

From the renormalized form (2) of the reaction and relaxation rates it follows that the rates of all reactions have a non-trivial dependence on the species densities, which differs greatly from the Guldberg and Waage equation. At the same time the chemical equilibrium condition expressed via the equilibrium constant for the spatially homogeneous case obeys the Guldberg and Waage law. This is the consequence of the equation (8) for $\tilde{a}_r^{(1)}$-coefficients. Equilibrium condition can be expressed as $\eta_r = 0$ for all reactions $r$, thus, the relationship between the equilibrium concentrations is a function only of the temperature. When $\eta_r = 0$, the RHS of the equations (8) are zero, thus, they have only trivial solution $\tilde{a}_r^{(1)} = 0$, so that $R_{a}^{ne} = 0$. From equation (8) it also follows that $a$-coefficients can be sought in the form $a_r^{(1)} = \sum \tilde{a}_r^{(1)} \eta_r$. Thus, the spatially homogeneous correction reads as $R_{a}^{ne} = \sum \tilde{a}_r^{(1)} \eta_r$. This means that the equilibrium conditions for each component assumes the condition $\eta_r = 0$ for every $r$, and no condition exists when only for one reaction its rate is non-zero, while for others reaction rates vanish. Mixture composition also impacts the reaction rate, therefore the reaction obtained from the experiment in one mixture cannot be applied for another. The latter two circumstances complicate obtaining the information concerning reaction rates from the experimental data. Integral brackets seem to be the only universal values for reaction rate determination under different conditions.

When calculated, the reaction rates need solving of the integral equations (5). This cannot be done by the variational methods (widely used in the kinetic theory) due to the non-symmetry of the kernel of the integral operator. Thus, the projection methods should be applied. The simplest version of such procedure has been demonstrated in the previous section.

Spatially inhomogeneous effects connected with the expansion/compression processes lead not only to the deviation of the system from its equilibrium, but to the change of the equilibrium condition. Guldberg and Waage law brakes down and the equilibrium condition becomes a function not only of the temperature, but of the species and velocity divergency. This makes calculation of the non-equilibrium reaction rates of great importance.

References

[1] Prigogine I, Xhouet E 1949 Physica 15 913–32
[2] Knight D, Longo J, Drikakis D, Gaitonde D, Lani A, Nompleis I, Reimann B and Walpot L 2012 Progress in Aerospace Sciences 48–49 8–26
[3] Hao J, Wang J, Zhenxun Gao Zh, Jiang Ch and Lee Ch 2017 Acta Astronautica 130 24–33
[4] Hao J, Wang J, Lee Ch 2017 Aerospace Science and Technology 67 433–42
[5] Kim J G, Boyd I D 2013 Chemical Physics 415 237–46
[6] Schwartzentruber T E, Boyd I D 2015 Progress in Aerospace Sciences 72 66–79
[7] Andrienko D A, Boyd I D 2017 Chemical Physics 491 74–81
[8] Robinson P J, Holbrook K A 1972 Unimolecular Reactions (Wiley-Interscience, London, New York, Sydney, Toronto)
[9] Stupochenko Ye V, Losev S A, Osipov A I 1967 Relaxation in Shock Waves (Springer-Verlag, New York)
[10] Kolesnichenko E, Gorbachev Yu 2013 Shock Waves 23 635–48
[11] Kolesnichenko E, Gorbachev Yu 2010 Applied Mathematical Modelling 34 3778–90
[12] Kolesnichenko E, Gorbachev Yu 2013 Applied Mathematical Modelling 37 5304–14
[13] Gorbachev Yu 2016 Applied Mathematical Modelling 40 10131–52
[14] Gorbachev Yu 2016 Proc. ICNAAM, AIP Conf. Proc. 1738
[15] Gorbachev Yu 2018 The eighth polyakhov’s reading: Proceedings of the International Scientific Conference on Mechanics 1959(1) 060005
[16] Kolesnichenko E G 1984 Fluid Dynamics 19 443–448