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Impact of vibrational non-equilibrium on chemical reaction rates. ⋆

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Abstract

We study non-equilibrium effects caused by dissociation and other chemical reactions in gas mixtures. For that, we employ a general algorithm for deriving a uniform asymptotic solution of the kinetic equation for spatially inhomogeneous reactive gas mixtures developed earlier by the authors. We show that chemical reactions lead to quasi-stationary vibrational distribution function that differs from the quasi-equilibrium one. Under such conditions, the approach based on introduction of reaction rate constants shall be revised. We obtained expressions for reaction rates of pure unimolecular processes that have a dependence on pressure in good agreement with the theory of unimolecular reactions. Considering both unimolecular and collisional mechanisms of elementary reactions leads to new dependencies of reaction rates on gas pressure. Parallel reactions are considered (when one molecule reacts with several others), and a strong correlation between these reactions is demonstrated in the non-equilibrium case. This correlation can be manifested as blocking of one reaction by another. It violates the mass action law.

ВЛИЯНИЕ КОЛЕБАТЕЛЬНОЙ НЕРАВНОВЕСНОСТИ НА СКОРОСТИ ХИМИЧЕСКИХ РЕАКЦИЙ

Исследуются неравновесные эффекты, обусловленные диссоциацией и другими химическими реакциями в газовых смесях. Для этого используется общий алгоритм построения асимптотического решения кинетического уравнения для пространственно неоднородных реагирующих газовых смесей, разработанный авторами ранее. Показано, что химические реакции приводят к квазистационарному колебательному распределению, отличающемуся от квазиравновесного. В этих условиях подход, основанный на введении понятия константы скорости реакции нуждается в пересмотре. Получены выражения для скоростей реакций чисто мономолекулярных процессов, которые имеют зависимость от давления, хорошо согласующуюся с теорией мономолекулярных реакций. Учет как мономолекулярного, так и столкновительного механизма элементарных реакций ведет к новой зависимости скоростей реакций от давления. Рассмотрены параллельные реакции (когда одна молекула реагирует с несколькими другими молекулами), и показана сильная корреляция между этими реакциями в неравновесном случае. Эта корреляция может проявляться как блокирование одной реакции другой. Это явление ведет к нарушению закона действующих масс.

Key words: Kinetic theory, reactive mixture, transport equations, non-equilibrium effects
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Ключевые слова: кинетическая теория, реагирующие газовые смеси, процессы переноса, неравновесные эффекты

1 Introduction.

In our previous paper [1] we developed a new general approach for deriving gas-dynamic equations from kinetic ones for reactive gases. This approach is based on elimination of fast variables and reduction of the system description. The fast variables are the parts of distribution functions. Their behavior is governed by the equations derived from generalized Boltzmann equations by change of variables. The reduced description is done in terms of slow variables for which the gas-dynamic equations are derived. The resulting equations contain extra terms in comparison with traditional ones. Determination of slow variables is based on the concept of so called approximate summational invariants (that include the exact ones). They determine a complete set of slow variables. Here, using this approach, we are going to describe some non-equilibrium effects in reactive gases. The non-equilibrium effects are the distinctions of new gas-dynamic equations from those obtained with quasi-equilibrium distribution functions. We define the quasi-equilibrium distribution functions as functions that maximize the entropy density of the system for fixed gas-dynamic variables.

Analysis of the gas-dynamic equations obtained in [1] shows that all non-equilibrium effects can be subdivided into three groups. The first group are the effects caused by the perturbation of quasi-equilibrium distribution function by the physical-chemical processes. Only these effects remain in the spatially homogeneous case. The second group consists of the terms proportional to the velocity divergence that arise in the expressions for the corresponding reaction rates. These effects are caused by expansion and compression of the gas. The first and second groups are represented in the zero order approximation. In the first order approximation the third group of

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non-equilibrium effects appears. It consists of terms in the expressions for the reaction rates, that are proportional to the scalar bilinear combinations of gas-dynamic variables gradients. Here we consider only the effects of the first group. Due to the additive contribution of all these terms to the gas-dynamic equations, they can be studied separately. The effects from the second and third group have been estimated in [2,3,4].

In this paper we study the non-equilibrium effects in chemical reactions induced by non-equilibrium vibrational distributions caused by the chemical reactions themselves. These effects are of the highest importance because they significantly influence the reaction rates, up to their vanishing. In Section 2 we calculate the non-equilibrium dissociation rate for a small admixture of dissociating molecules in noble gas mixture in a one-temperature regime. It was previously calculated in the theory of unimolecular reactions [5,6], but only for unimolecular dissociation mechanism. Unlike the previous treatments, both unimolecular and collisional mechanisms of dissociation are considered here. This leads to new results concerning the dependence of the dissociation rate on the gas mixture pressure. Generalization of such system description for the spatially inhomogeneous case is discussed. A case of arbitrary concentration of the dissociating gas is also studied. An iterative procedure for the distribution function and reaction rates calculation is proposed. In section 3 the peculiarities of the exchange reactions' pressure behavior is briefly considered. In Section 4 more complex system with two parallel chemical reactions is analyzed. The effect of interdependency of different reactions in the non-equilibrium case is shown. It means the violation of the mass action law. This makes it very difficult to obtain reaction rates from experimental data. Appendix A contains expressions for the collision integrals. It is shown that the kinetic equation with these integrals satisfies the H-theorem. In Appendix B equations for vibrational population densities are derived.

2 Thermal Dissociation Reactions.

2.1 State-of-the-art.

Let us consider the generalized Boltzmann equation

$$\frac{\partial F_\alpha}{\partial t} + \mathbf{v}_\alpha \cdot \nabla F_\alpha = \frac{1}{\varepsilon} I_\alpha(F). \tag{1}$$

Here F_α, I_α and $\mathbf{v}_\alpha$ is the distribution function, the collisional integral and the velocity of the molecule of sort α, ε is the ratio of characteristic time of inelastic process to characteristic gas-dynamic time. Slow variables are introduced as

$$\Gamma_i = \langle \psi_i, F \rangle\,, \qquad \langle \psi, \varphi \rangle = \sum_\alpha \sum_{k_\alpha} \int d\mathbf{v}_\alpha \psi_\alpha\left(\mathbf{v}_\alpha, k_\alpha\right) \varphi_\alpha\left(\mathbf{v}_\alpha, k_\alpha\right). \tag{2}$$

Here k_α are quantum numbers of species α and ψ_i is the set of approximate summational invariants (ASI) that is defined by the condition

$$\langle \psi_i, I\left(F\right)\rangle \leq O\left(\varepsilon\right). \tag{3}$$

As a result the distribution function can be treated as a function of t, $\mathbf{r}$ and Γ_i and time and spatial derivations should be rewritten as $\dfrac{\partial F_\alpha}{\partial t} \to \dfrac{\partial F_\alpha}{\partial t} + \sum_i \dfrac{\partial F_\alpha}{\partial \Gamma_i}\dfrac{\partial \Gamma_i}{\partial t}$ and $\nabla F_\alpha \to \nabla F_\alpha + \sum_i \dfrac{\partial F_\alpha}{\partial \Gamma_i}\nabla\Gamma_i$ respectively. Multiplying eq. (1) by ψ_i and calculating the scalar products we obtain the equations for Γ_i. Substituting them into the last equation we get

$$\frac{\partial F_\alpha}{\partial t} = \frac{1}{\varepsilon}\left(I_\alpha(F) - \sum_{i=1}^{M}\frac{\partial F_\alpha}{\partial \Gamma_i}\langle \psi_i, I\left(F\right)\rangle\right) - \mathbf{v}\cdot\nabla F_\alpha + \sum_{i=1}^{M}\frac{\partial F_\alpha}{\partial \Gamma_i}\left(\nabla\cdot\langle \mathbf{v}\psi_i, F\rangle - \mathbf{v}\cdot\nabla\Gamma_i\right).$$

Here and further all time and spatial derivations correspond to the direct time and spatial co-ordinate dependence of the corresponding functions. This equation coincides with the commonly used only when all ψ_i are exact summational invariants (ESI). It shows the main difference between the systems that are described by slow variables originated from exact and approximate summational invariants. Then it is convenient to represent $F_\alpha = F^0_\alpha(\{\Gamma_i\}) + \Phi_\alpha$, where the first item depends only on slow variables.

Following the formalism of our previous paper [1], we choose $F^0_\alpha = F^{(qe)}_\alpha(\Gamma_1, \ldots, \Gamma_M)$, where quasi-equilibrium distribution functions $F^{(qe)}_\alpha$ maximize the entropy density for a fixed set of slow variables: $F^{(qe)}_\alpha = \exp\left(\ln s_\alpha\left(k_\alpha\right) - \sum_{i=1}^{M}\gamma_i\psi_{i\alpha}\left(\mathbf{v}_\alpha, k_\alpha\right)\right)$. Here $s_\alpha(k_\alpha)$ are corresponding statistical weights, γ_i are determined by the relations $\Gamma_i = \left\langle \psi_i, F^{(qe)}\right\rangle$ and Φ_α should satisfy relations $\langle\psi_i, \Phi\rangle = 0$. Equations for slow variables then have the form

$$\frac{\partial \Gamma_i}{\partial t} = \frac{1}{\varepsilon}\left\langle \psi_i, I\left(F^{(qe)} + \Phi\right)\right\rangle - \nabla\cdot\left\langle \mathbf{v}\psi_i, \left(F^{(qe)} + \Phi\right)\right\rangle. \tag{4}$$

Further we follow the methodology of section 4 presented in [1], where a simplified case is considered with a "week" non-equilibrium situation when Φ_α function is assumed to be of the order of ε. For the one-temperature flow $F^{(qe)}_\alpha$ is a Maxwell-Boltzmann distribution function. It should be mentioned that the collisional integral $I_\alpha(F)$ calculated with $F^{(qe)}_\alpha$ does not vanish since this distribution contains not only exact summational invariants.

In the dimensionless form, the equation for the lowest order correction for the distribution function, $\Phi^{(0)}$, (see Eq (22) in paper [1]) can be written as

$$J'_{F^{(qe)}}(F^{(qe)})\Phi^{(0)} = -\frac{1}{\varepsilon}J_{F^{(qe)}}\left(F^{(qe)}\right) + \sum_{i=1}^{M}\frac{\partial F^{(qe)}}{\partial \Gamma_i}\left[\mathbf{v}\cdot\nabla\Gamma_i - \nabla\cdot\left\langle \mathbf{v}\psi_i, F^{(qe)}\right\rangle\right]. \tag{5}$$

Here summation over i denotes the summation over all slow variables (2), $J'_F(G)$ is the modified collision operator $J_F(G)$ linearized over G, and

$$J_{F^{(qe)}}(G) = I(G) - \sum_{i=1}^{M} \frac{\partial F^{(qe)}}{\partial \Gamma_i} \langle \psi_i, I(G) \rangle. \tag{6}$$

As it was discussed in [1], from the structure of the equation (5) it follows that $\Phi^{(0)}$ can be represented as a sum of terms of three types

$$\Phi^{(0)}_{\alpha} = \Phi^{(0)}_{1\alpha} + \Phi^{(0)}_{2\alpha} \nabla \cdot \mathbf{u} + \Phi^{(0)}_{3\alpha} \left(\mathbf{c}_\alpha \mathbf{c}_\alpha - \frac{1}{3} \mathbf{c}^2_\alpha \right) : \nabla \mathbf{u} + \Phi^{(0)}_{4\alpha} \mathbf{c}_\alpha \cdot \nabla E$$

$$+ \sum_{i=1}^{N} \Phi_{n_i \alpha} \mathbf{c}_\alpha \cdot \nabla\ n_i + \sum_{i=N+5}^{M} \Phi_{\Gamma_i \alpha} \mathbf{c}_\alpha \cdot \nabla \Gamma_i.$$

The first term, $\Phi^{(0)}_{1\alpha}$, is independent on the gas-dynamic variables gradients and we call it a scalar one. The second one, containing $\Phi^{(0)}_{2\alpha}$, is proportional to the mixture mass velocity divergence. The terms of the third type are proportional to the linear combination of gradients of gas-dynamic variables. Due to such an additive structure, in this paper we consider only the scalar part responsible for the physical-chemical processes. The corresponding equation for the dissociating gas has the form

$$J'_{F^{(qe)}_1} \left(F^{(qe)}_1 \right) \Phi^{(0)}_{1,1} = -\frac{1}{\varepsilon} J_{F^{(qe)}_1} \left(F^{(qe)}_1 \right). \tag{7}$$

The terms of the second and third types are responsible for the spatial inhomogeneity effects. Considering these effects makes the proposed method generic, overcoming the limitations of all the previous approaches describing only the spatially homogeneous situations [6,8].

To check the method, we start with the well studied problem of a small admixture of dissociating molecules in noble gas mixture. The kinetic equations for such a mixture have the form

$$\frac{\partial F_1}{\partial t} + \mathbf{v}_1 \cdot \nabla F_1 = I_1 = I^u_1 + I^c_1 + I^{nr}_1, \tag{8}$$

$$\frac{\partial F_\alpha}{\partial t} + \mathbf{v}_\alpha \cdot \nabla F_\alpha = I_\alpha, \quad \alpha = 2, ..., 5. \tag{9}$$

Here F_α, I_α and $\mathbf{v}_\alpha$ is the distribution function, the collisional integral and the velocity of the molecule of sort α, subindex 1 denotes the dissociating species, subindexes 2 and 3 denote the noble gas species and subindexes 4 and 5 denote the dissociation reaction products. The first term in the RHS of equation (8), I^u_1, describes the metastable molecules decay via unimolecular process and their formation due to dissociation products agglomeration. The second term, I^c_1, describes the direct dissociation and recombination reactions occurring during the three-particle collisions. The third term, I^{nr}_1, corresponds to the nonreactive dual collisions. The detailed representation of all collision integrals is adduced in Appendix A.

For a small admixture of dissociating molecules, the set of equations (8)-(9) can be simplified. The concentrations of these molecules and dissociation products are small, therefore the collisions of these molecules and dissociation products with each other can be neglected. This leads to the following simplifications of the set of kinetic equations: recombination in terms I_1^u and I_1^c (proportional to $F_4 F_5$ product) is omitted. The summation in I_1^{nr} and in I_1^c is reduced to $\alpha = 2, 3$. That means that only the collisions of admixture with noble gas particles are considered. In equations for noble gases ($\alpha = 2, 3$) only collisions of these gases among each other are considered. Distributions of dissociation products ($\alpha = 4, 5$) are assumed to be Maxwell-Boltzmann and corresponding equations are omitted.

2.2 Small concentration of dissociating molecules.

Before solving equation (7) let us chose the terms in which the system will be described, namely the list of slow variables. According to the definition (2), they are defined via the set of approximate summational invariants (ASI) (3), that in turn are determined by the small parameter ε. This parameter we define as the ratio of the characteristic chemical time, τ_{ch}, to the gas-dynamical time, τ_G. The latter is determined by the flow parameters $\tau_G = L/U$, where $L \sim \min_i \{\Gamma_i / \max |\nabla \Gamma_i|\}$, and $U = c(1 + S)$ is the gas-dynamic velocity scale. Here c is sound speed, $S = u/c$, and u is the gas-dynamic velocity [1]. While studying the one-temperature flow, one assumes that the following ASI satisfy condition (3)

$$\delta_{\alpha,1}, \quad m_\alpha \mathbf{v}_\alpha, \qquad e_\alpha^{(T)}(\mathbf{v}_\alpha) + e_\alpha^{(int)}(k_\alpha), \tag{10}$$

where $\delta_{\alpha,\beta}$ is a Kronecker symbol, $e_\alpha^{(T)} = m_\alpha \mathbf{v}_\alpha^2/2$ and $e_\alpha^{(int)}$ are translational and internal energies of the molecules of sort α respectively, and k_α are the quantum numbers determining the internal energy of the molecule. Corresponding gas-dynamic variables defined according to (2) are number densities of species, mean mixture momentum and mean total energy.

For molecule energy and statistical weight we use expressions

$$\begin{gathered}
e_\alpha(\mathbf{v}_\alpha, k_\alpha) = e_\alpha^{(0)} + e_\alpha^{(T)}(\mathbf{v}_\alpha) + e_\alpha^{(int)}(j_\alpha, q_\alpha), \\
e_\alpha^{(int)}(j_\alpha, q_\alpha) = e_\alpha^{(R)}(j_\alpha) + e_\alpha^{(RV)}(j_\alpha, q_\alpha) + e_\alpha^{(V)}(q_\alpha), \\
e_\alpha^{(TRV)}(\mathbf{v}_\alpha, j_\alpha, q_\alpha) = e_\alpha^{(T)}(\mathbf{v}_\alpha) + e_\alpha^{(R)}(j_\alpha) + e_\alpha^{(RV)}(j_\alpha, q_\alpha), \\
s_\alpha(k_\alpha) = s_\alpha^{(R)}(j_\alpha) s_\alpha^{(RV)}(j_\alpha, q_\alpha) s_\alpha^{(V)}(q_\alpha),
\end{gathered} \tag{11}$$

where $k_\alpha = (j_\alpha, q_\alpha)$, $e_\alpha^{(0)}$ is the minimum of the potential energy and T, R, and V denotes translational, rotational and vibrational degrees of freedom respectively. While solving equation (7) we shall neglect the perturbations of Maxwell-Boltzmann distributions for translational and rotational degrees of freedom for all components. Then the distribution functions can be written as

$$F_\alpha = F_\alpha^{(qe)\,TR} X_\alpha, \tag{12}$$

where

$$\begin{gathered}
F_\alpha^{(qe)\,TR}(\mathbf{v}_\alpha, j_\alpha, q_\alpha) = \frac{s_\alpha^{(R)}(j_\alpha) s_\alpha^{(RV)}(j_\alpha, q_\alpha)}{Q_\alpha^{(TR)}(q_\alpha)} \exp\left[-\frac{e_\alpha^{(TRV)}(\mathbf{v}_\alpha, j_\alpha, q_\alpha)}{kT}\right], \\
Q_\alpha^{(TR)}(q_\alpha) = \sum_{j_\alpha} \int d\mathbf{v}_\alpha s_\alpha^{(R)}(j_\alpha) s_\alpha^{(RV)}(j_\alpha, q_\alpha) \exp\left[-\frac{e_\alpha^{(TRV)}(\mathbf{v}_\alpha, j_\alpha, q_\alpha)}{kT}\right].
\end{gathered} \tag{13}$$

F_α is normalized to the number density n_α of particles of sort α. $F_\alpha^{(qe)\,TR}$ is normalized to the unity. Thus we have $\sum_{j_\alpha} \int d\mathbf{v}_\alpha F_\alpha = X_\alpha(q_\alpha)$ and $X_\alpha(q_\alpha)$ can be interpreted as a vibrational population density. Further following tradition we shall write $X_\alpha(q_\alpha) \equiv X_{\alpha,q_\alpha}$.

Now let us consider equation (7). For simplicity in this article we study the case of uncoupled rotation and vibration ($e_\alpha^{(RV)}(j_\alpha, q_\alpha) = 0$) and restrict ourselves with consideration of diatomic molecules when $s^{(V)} = 1$. After substitution of functions (12) into equation (7) and integration over $\mathbf{v}_1$ and summation over j_1 one obtains an equation for $X_{1,q,1}^{(0)} = \sum\limits_{j_1} \int d\mathbf{v}_1 \Phi_{1,1}^{(0)}(\mathbf{v}_1, q)$ (see Appendix B). While calculating the scalar product in the modified collisional operator (6) the specific set of ASI (10) should be taken into account. Two last functions are exact summational invariants which means that the scalar product in (6) is non-zero only for terms containing derivations over number densities of species $\Gamma_{n_\alpha} = n_\alpha$. Corresponding products lead to the terms containing reaction rates

$$R_\alpha = \left\langle \delta_{\alpha,\beta}, I\left(F_\beta^{(qe)}\right)\right\rangle.$$

For non-reacting species ($2, 3$ in our case) $\delta_{\alpha,\beta}$ is an exact summational invariant and therefore corresponding rates vanishes ($R_2 = R_3 = 0$).

For further analysis we will account presence of other exact summational invariants, namely the total number of atoms in all species. Let us denote molecules of different species as $A_1, ..., A_\alpha, ..., A_N$, and the atoms (elements), that are the parts of molecule A_α as $A_{\alpha,k}$, $k = 1, ..., K$. Then the molecule can be represented as $\zeta_{\alpha,1} A_{\alpha,1}, ..., \zeta_{\alpha,K} A_{\alpha,K}$, where $\zeta_{\alpha,k}$ is the number of atoms of sort k in the molecule of sort α (for those molecules that don't contain element k, $\zeta_{\alpha,k} = 0$). Since the number of particles of each chemical element is kept constant during the chemical reactions, linear combinations of ASI $\sum_\beta \zeta_{\beta,k} \delta_{\alpha,\beta}$ are exact summational invariants for $k = 1, ..., K$ [7]. As they are the expressed via ASI, they do not produce new gas-dynamic variables, but leads to K linear relations between chemical reaction rates that reflects the chemical elements conservation

$$\sum_\alpha \zeta_{\alpha,k} R_\alpha = 0, \qquad k = 1, ...K. \tag{14}$$

After multiplying this equation over atomic mass μ_k and summation over elements one obtains the mass conservation law ($m_\alpha = \sum_k \zeta_{\alpha,k}\mu_k$)

$$\sum_\alpha m_\alpha R_\alpha = 0. \tag{15}$$

For our case of dissociation, this leads to two additional relations

$$R_1 + R_4 = 0, \qquad R_1 + R_5 = 0.$$

that in turn leads to the relation $R_4 = R_5 = -R_1$ and is used in our following analysis. As a result the term that contains the derivations over number densities has the form

$$\left(\frac{\partial X_{1,n}}{\partial n_1} - \frac{\partial X_{1,n}}{\partial n_4} - \frac{\partial X_{1,n}}{\partial n_5}\right) R_1 \equiv S_1(X_{1,n}) R_1. \tag{16}$$

Summarizing all previous reasonings and assuming only one-quantum vibrational transitions, one gets the following set of dimensionless equations

$$\begin{gathered}\varepsilon\left(-(1-\delta_{q,0})j_{q-1}(X^{(0)}) + (1-\delta_{q,q_m})j_q(X^{(0)}) - P_{q,d}X^{(0)}_{1,q} - S(X^{(qe)}_{1,q})R^{(0)}\right)\\ = (1-\delta_{q,0})j_{q-1}(X^{(qe)}) - (1-\delta_{q,q_m})j_q(X^{(qe)}) + P_{q,d}X^{(qe)}_{1,q} + S(X^{(qe)}_{1,q})R^{(qe)},\end{gathered} \tag{17}$$

$$j_q\left(X\right) = P_{q+1,q}X_{1,q+1} - P_{q,q+1}X_{1,q},$$

where q_m is the maximum vibrational quantum number. Here and further for simplification of notations we omit the last subscript 1 in $X^{(0)}_{1,q,1}$, in S and in R_1, and by definition

$$R^{(qe)} = \left\langle \delta_{\alpha,1}, I\left(F^{(qe)}\right)\right\rangle = -\sum_{q=0}^{q_m} P_{q,d}X^{(qe)}_{1,q},$$

$$R^{(0)} = \left\langle \delta_{\alpha,1}, I'\left(F^{(qe)}\right)\Phi^{(0)}\right\rangle = -\sum_{q=0}^{q_m} P_{q,d}X^{(0)}_{1,q},$$

where $P_{q,d}$ are the dissociation probabilities of the molecule in vibrational state q.

$$P_{q,q'} = \sum_{\alpha=2}^{3}\sum_{\substack{j,j'\\ j\neq j'}}\sum_{k_\alpha,k'_\alpha}\int d\mathbf{v}_\alpha d\mathbf{v}_1 d\mathbf{v}'_\alpha d\mathbf{v}'_1 F_1^{(qe)\,TR}F_\alpha^{(qe)\,TR}$$

$$\times W^{1,\alpha}_{1,\alpha}\left(\mathbf{v}_1, k_1, \mathbf{v}_\alpha, k_\alpha | \mathbf{v}'_1, k'_1, \mathbf{v}'_\alpha, k'_\alpha\right)$$

are the averaged vibrational-translational (VT) transition probabilities and W are transition probabilities. They satisfy the detailed balance relation (see Appendix B)

$$P_{q,q'} = P_{q',q} \exp\left(-\frac{e_1^{(V)}(q') - e_1^{(V)}(q)}{kT}\right), \tag{18}$$

Quasi-equilibrium vibrational population by definition is represented as

$$X_{1,q}^{(qe)} = n_1 \chi_q / Q_1, \qquad \chi_q = \exp\left(-\frac{e_1^{(V)}(q)}{kT}\right), \qquad Q_1 = \sum_{q=0}^{q_m} \chi_q, \tag{19}$$

where Q_1 is the vibrational statistical sum of molecules of type 1.

By setting in (17) $X^{(qe)} + \varepsilon X^{(0)} = X$, $R^{(qe)} + \varepsilon R^{(0)} = R$, and transforming to dimensional variables we obtain

$$(1 - \delta_{q,0}) j_{q-1}(X) - (1 - \delta_{q,q_m}) j_q(X) + P_{q,d} X_{1,q} + S(X_{1,q}^{(qe)}) R = 0. \tag{20}$$

By summing equation for $q = 0$ and equation for $q = 1$, and repeating this procedure for $q = 2$, etc., we obtain the recurrence relation

$$j_q(X) - \sum_{r=0}^{q} \left(P_{r,d} X_{1,r} + RS(X_{1,r}^{(qe)})\right) = 0, \qquad q = 0, ..., q_m - 1.$$

Summation of all the equations leads to the expression for the total dissociation rate R

$$R = -\sum_{r=0}^{q_m} P_{r,d} X_{1,r}. \tag{21}$$

Here the normalizing relationships $\sum_{q=0}^{q_m} X_{1,q}^{(qe)} = n_1$ and $S(n_1) = 1$ are taken into account. Relationship (21) means that the set of equations for $X_{1,q}$ is degenerate and normalizing relation is used further for closing the problem.

For further algebra simplification we make the assumption that the dissociation occurs only from the highest vibration level q_m, so that $P_{q,d} = \delta_{q,q_m} P_{q_m,d}$ [6]. As a result the recurrence relations are reduced to

$$j_q(X) - \sum_{r=0}^{q} RS(X_{1,r}^{(qe)}) = 0, \qquad q = 0, ..., q_m - 1, \tag{22}$$

and the sum in expression (21) is reduced to the only one last item.

From equations (22) one obtains

$$X_{1,q+1} = a_q X_{1,q} + b_q, \tag{23}$$

$$a_q = \frac{P_{q,q+1}}{P_{q+1,q}}, \qquad b_q = \frac{1}{P_{q+1,q}} \sum_{r=0}^{q} RS(X_{1,r}^{(qe)}) \equiv \frac{R}{P_{q+1,q}} S(\Theta^{(q)}),$$

$$\Theta^{(q)} = \sum_{r=0}^{q} X_{1,r}^{(qe)}, \qquad \Theta^{(q_m)} = n_1, \qquad S(\Theta^{(q_m)}) = 1.$$

Taking into account the detailed balance relationships (18), the expression for a_q can be rewritten in the form $a_q = \chi_{q+1}/\chi_q$. Solution of the chain of recurrent equations can be expressed as

$$X_{1,q+1} = \prod_{r=0}^{q} a_r X_{1,0} + \sum_{s=0}^{q} b_s \prod_{r=s+1}^{q} a_r, \tag{24}$$

thus

$$X_{1,q} = \frac{\chi_q}{\chi_0} X_{1,0} + Rc_q, \qquad c_q = \sum_{r=0}^{q-1} \frac{\chi_q}{\chi_{r+1}} \frac{S(\Theta^{(r)})}{P_{r+1,r}}. \tag{25}$$

$X_{1,0}$ is determined from the normalization condition:

$$n_1 = \sum_{q=0}^{q_m} X_{1,q} = \sum_{q=0}^{q_m} \frac{\chi_q}{\chi_0} X_{1,0} + R \sum_{q=1}^{q_m} c_q = \frac{Q_1}{\chi_0} X_{1,0} + RC,$$

that gives

$$X_{1,0} = \chi_0 \left(n_1 - RC\right) Q_1^{-1}, \qquad C = \sum_{q=1}^{q_m} c_q.$$

As a result

$$X_{1,q} = n_1 \frac{\chi_q}{Q_1} + R\left[c_q - C\frac{\chi_q}{Q_1}\right]. \tag{26}$$

Finally, using this vibrational distribution function, for dissociation rate (21) we obtain

$$\begin{aligned} R &= -\frac{P_{q_m,d} n_1 \chi_{q_m} Q_1^{-1}}{1 + P_{q_m,d}\left[c_{q_m} - C\chi_{q_m} Q_1^{-1}\right]} \\ &= -\frac{P_{q_m,d} X_{1,q_m}^{(qe)}}{1 + P_{q_m,d}\left[c_{q_m} - C X_{1,q_m}^{(qe)} n_1^{-1}\right]}. \end{aligned} \tag{27}$$

This expression slightly differs from that obtained by Stupochenko et al [6], and coincides with it if the normalization factor is accounted with the same accuracy as in [6]. It means that $C\chi_{q_m}/Q_1$ is neglected in comparison with c_{q_m}, and $S(\Theta^{(r)})$ are replaced by $\Theta^{(r)}/n_1$. S-factor for the dissociation reactions (see (16)) can be represented as

$$S(X_{1,g}^{(qe)}) = \frac{X_{1,g}^{(qe)}}{n_1}\left(1 + \frac{n_1\left(e_1^{(V)}(g) - E^{(V)}\right)}{kT} S(\ln(kT))\right), \tag{28}$$

where $E^{(V)} = \sum\limits_{q=0}^{q_m} e_1^{(V)}(q) X_{1,g}^{(qe)}/n_1$.

It reflects the chemical reaction affect on the temperature and will be analyzed in more details elsewhere.

Substituting expression (27) into (26), after some algebra one obtains

$$X_{1,q} = \frac{n_1\left(\chi_q + P_{q_m,d}(c_{q_m}\chi_q - c_q\chi_{q_m})\right)}{Q_1\left(1 + P_{q_m,d}\left(c_{q_m} - C\chi_{q_m}Q_1^{-1}\right)\right)}. \tag{29}$$

From this expression one can see that in the limits of low and high vibrational quantum numbers q this distribution is close to Boltzmann distribution with the same temperature, but with different normalizing factors, with the ratio of $1 + P_{q_m,d}c_{q_m}$.

Now let us analyze the expression (27) in the limits of low and high pressure taking into account that the vibrational transition probabilities are proportional to the number densities of the noble gases

$$P_{q,q-1} = p^{(2)}_{q,q-1}n_2 + p^{(3)}_{q,q-1}n_3 = [M]\left(p^{(2)}_{q,q-1}\xi_2 + p^{(3)}_{q,q-1}\xi_3\right). \tag{30}$$

Here n_α, $[M] = \sum_\alpha n_\alpha$, ξ_α $(\alpha = 2,3)$ are number densities of the noble gases, total number density, and number concentrations $(n_\alpha = \xi_\alpha[M])$ of noble gases respectively. Then $c_N \approx c'_N[M]^{-1}$, $C \approx C'[M]^{-1}$, where primed parameters are pressure independent. Besides, let us represent the dissociation probability as a sum of probabilities for unimolecular and collisional process that correspond to collision integrals I^m and I^c of equation (8) respectively

$$P_{q,d} = P^{(u)}_{q,d} + P^{(c)}_{q,d} = P^{(u)}_{q,d} + p^{(c)}_{q,d}[M] = P^{(u)}_{q,d} + \left(p^{(c,2)}_{q,d}\xi_2 + p^{(c,3)}_{q,d}\xi_3\right)[M], \tag{31}$$

where the probability of unimolecular decay is independent of the gas density, while collisional probability is proportional to $[M]$. After substitution of formulas (30) and (31) into the expression for dissociation rate (27) for low pressure limit $([M] \to 0)$ one obtains

$$R_0 = -\frac{\xi_1\chi_{q_m}Q_1^{-1}}{c'_{q_m} - C'\chi_{q_m}Q_1^{-1}}[M]^2. \tag{32}$$

While deriving the last expression it was assumed that $P^{(u)}_{q,d} \neq 0$. That means that the rate (32) is determined by the unimolecular mechanism. As it was already mentioned in [6], the reaction rate in this limit does not depend on the dissociation probability.

For high pressure limit $([M] \to \infty)$ expression (27) transforms to

$$\begin{gathered} R_\infty = -\frac{\xi_1\chi_{q_m}Q_1^{-1}[M]}{1 + \left(p^{(c,2)}_{q_m,d}\xi_2 + p^{(c,3)}_{q_m,d}\xi_3\right)\left(c'_{q_m} - C'\chi_{q_m}Q_1^{-1}\right)} \\ \times\left[\left(p^{(c,2)}_{q_m,d}\xi_2 + p^{(c,3)}_{q_m,d}\xi_3\right)[M] + \frac{P^{(u)}_{q_m,d}}{1 + \left(p^{(c,2)}_{q_m,d}\xi_2 + p^{(c,3)}_{q_m,d}\xi_3\right)\left(c'_{q_m} - C'\chi_{q_m}Q_1^{-1}\right)}\right]. \end{gathered} \tag{33}$$

The collisional part of the dissociation probability $P^{(c)}_{N,d}$ is disregarded by the majority of investigators. In this case R_∞ transforms to the equilibrium one which equals to $P^{(u)}_{N,d}\chi_N Q_1^{-1} n_1$. As we can see from (33), it is not the general case. It can be explained as follows. For the high pressure limit the collisionally induced processes prevail over the unimolecular ones (see (31)). At the same time the ratio of the collisional reaction rate and the vibration relaxation rate is pressure independent, therefore it does not vanish at high pressures. It should be pointed out that there is no reason for neglecting the collisionally induced processes.

As pressure grows, the thermal dissociation mechanism changes from the unimolecular one to the collisional one.

Thus the approach suggested in [1] allows to reproduce the following well-proved fact of the chemical physics: the dissociation reaction mechanism is modified when passing from low to high pressures [5,9]. This allows to conclude that from the physical point of view it is an adequate generalization of the Chapman-Enskog method for the gases with internal degrees of freedom.

One more feature of the dissociation process should be mentioned here. Conventional expression for the dissociation rate in the presence of two noble gases is $R = -K_2 n_2 n_1 - K_3 n_3 n_1$, where K_2 and K_3 are the rate constants in gas 2 and in gas 3 respectively. On the other hand, from equation (27) with the probability (30), it follows that non-equilibrium rate depends on the noble gas density in a much more complicated form. This means that in non-equilibrium situation $(P_{q_m,d}(c_{q_m} - C X^{(qe)}_{1,q_m} n_1^{-1}) \geq 1)$ the reaction rate R is not a linear function of the mixture species concentrations and in general could not be obtained from the individual data for different component rates. It should be mentioned here that both c_{q_m} and C are complex functions of noble gas concentrations.

2.3 Arbitrary concentration of dissociating molecules.

If the concentration of dissociating molecules is not small the vibration-vibration (VV) energy transfer as well as recombination should be taken into account [8]. Here we consider only a one-temperature case.

We describe the system in terms of gas-dynamic (slow) variables: species densities, mean bulk velocity, and mean total mixture energy. We assume that the perturbation of the translational-rotational distribution function of the dissociating gas is negligible, therefore the Maxwell-Boltzmann distribution for them can be used. For simplicity, we use the assumption that the perturbation of the Maxwell-Boltzmann distribution of all dissociation products is also negligible. Then equation (7) can be reduced to the equation for vibrational population densities $X_{1,q}$ of species 1, as it was done in Section 2.2. The vibrational collisional operator $I_1^{(V)}$ (operator I_1 integrated over velocities $\mathbf{v}_1$ and summed over rotation quantum numbers j_1) can be written as

$$I_1^{(V)} = I_1^{(ch)} + I_1^{(VT)} + I_1^{(VV)},$$

where superscripts ch, VT and VV denote chemical reactions (both unimolecular and collisional), to vibration-translation and vibration-vibration transitions respectively. In this case

$$I_{1,q}^{(VT)} = \sum_{r\neq q} \left(P_{r,q}X_{1,r} - P_{q,r}X_{1,q}\right),$$

$$I_{1,q}^{(VV)} = \sum_{s,l,r\neq q} \left(Q_{r,q}^{s,l}X_{1,r}X_{1,s} - Q_{q,r}^{l,s}X_{1,q}X_{1,l}\right)$$

$$\equiv \sum_{r\neq q} \left(Q_{r,q}(X_1)X_{1,r} - Q_{q,r}(X_1)X_{1,q}\right).$$

Due to the detailed balance relation one has

$$P_{r,q}X_{1,r}^{(qe)} = P_{q,r}X_{1,q}^{(qe)}, \qquad Q_{r,q}^{s,l}X_{1,r}^{(qe)}X_{1,s}^{(qe)} = Q_{q,r}^{l,s}X_{1,q}^{(qe)}X_{1,l}^{(qe)}, \tag{34}$$

where $X^{(qe)}$ was defined in (19). For simplicity we consider only one-quantum transitions. Then

$$P_{r,q} = \left(\delta_{r,q+1} + \delta_{r,q-1}\right)P_{r,q}, \qquad Q_{r,q}^{s,l} = \left(\delta_{r,q+1}\delta_{l,s+1} + \delta_{r,q-1}\delta_{l,s-1}\right)Q_{r,q}^{s,l},$$

and

$$I_{1,q}^{(VT)} = (1-\delta_{q,0})\left(P_{q-1,q}X_{1,q-1} - P_{q,q-1}X_{1,q}\right)$$

$$-(1-\delta_{q,q_m})\left(P_{q,q+1}X_{1,q} - P_{q+1,q}X_{1,q+1}\right),$$

$$I_{1,q}^{(VV)} = (1-\delta_{q,0})\sum_{l}^{q_m-1}\left(Q_{q-1,q}^{l+1,l}X_{1,q-1}X_{1,l+1} - Q_{q,q-1}^{l,l+1}X_{1,q}X_{1,l}\right)$$

$$+(1-\delta_{q,q_m})\sum_{l}^{q_m-1}\left(Q_{q+1,q}^{l,l+1}X_{1,q+1}X_{1,l} - Q_{q,q+1}^{l+1,l}X_{1,q}X_{1,l+1}\right)$$

$$\equiv (1-\delta_{q,0})Q_{q-1,q}(X)X_{1,q-1} - Q_{q,q-1}(X)X_{1,q}$$

$$-(1-\delta_{q,q_m})\left(Q_{q,q+1}(X)X_{1,q} - Q_{q+1,q}(X)X_{1,q+1}\right),$$

where q_m is the highest vibrational level.

Introducing effective transition probabilities

$$\tilde{P}_{i,j}(X_1) = P_{i,j} + Q_{i,j}(X_1),$$

one can get the following expression for the collisional operator $I^{(V)}_{1,q}(X_1)$

$$I^{(V)}_{1,q} = (1-\delta_{q,0})\tilde{j}_{q-1}(X_1)X_1 - (1-\delta_{q,q_m})\tilde{j}_q(X_1)X_1 - \delta_{q,q_m}\left(P_{q,d}X_{1,q} - P_{q,r}n_4n_5\right),$$

$$\tilde{j}_q(X)Y = \tilde{P}_{q+1,q}(X)Y_{1,q+1} - \tilde{P}_{q,q+1}(X)Y_{1,q},$$

where $P_{q_m,d}$ is dissociation probability of the molecule in state q_m, and $P_{q_m,r}$ is recombination probability of the dissociation products to initial molecule in state q_m respectively, subindexes 4 and 5 denote the dissociation products. $P_{q,d(r)}$ with $q < q_m$ are assumed to be negligible. It should be mentioned that according to (34) one has $\tilde{j}_q(X^{(qe)})X^{(qe)} = 0$.

Since the modified collision operator (6) contains only one nonzero term in the sum over the approximate summational invariants, which corresponds to $\psi_i = \delta_{i,j}$, equation (7) for the scalar part of the perturbation of the distribution function in dimensionless form can be written as

$$\varepsilon\Bigg(-(1-\delta_{q,0})\tilde{j}_{q-1}(X_1^{(qe)})X_1^{(0)} + (1-\delta_{q,q_m})\tilde{j}_q(X_1^{(qe)})X_1^{(0)} + \delta_{q,q_m}P_{q,d}X^{(0)}_{1,q}$$

$$+S_1\left(X^{(qe)}_{1,q}\right)R_1^{(0)} - (1-\delta_{q,0})\tilde{j}'_{q-1}(X_1^{(0)})X_1^{(qe)} + (1-\delta_{q,q_m})\tilde{j}'_q(X_1^{(0)})X_1^{(qe)}\Bigg) \tag{35}$$

$$= (1-\delta_{q,0})\tilde{j}_{q-1}(X_1^{(qe)})X_1^{(qe)} - (1-\delta_{q,q_m})\tilde{j}_q(X_1^{(qe)})X_1^{(qe)}$$

$$-\delta_{q,q_m}\left(P_{q,d}X^{(qe)}_{1,q} - P_{q,r}n_4n_5\right) - S_1\left(X^{(qe)}_{1,q}\right)R_1^{(qe)},$$

$$\tilde{j}'_q(X)Y = Q_{q+1,q}(X)Y_{1,q+1} - Q_{q,q+1}(X)Y_{1,q}.$$

Here $S_1(X)$ is defined in (16) and, as in Section 2.2,

$$R_1^{(qe)} = \left\langle \delta_{\alpha,1}, I\left(X_1^{(qe)}\right)\right\rangle = -\textstyle\sum_{q=0}^{q_m}\left(P_{q,d}X^{(qe)}_{1,q} - P_{q,r}n_4n_5\right),$$

$$R_1^{(0)} = \left\langle \delta_{\alpha,1}, I'\left(X_1^{(qe)}\right)X_1^{(0)}\right\rangle = -\textstyle\sum_{q=0}^{q_m} P_{q,d}X^{(0)}_{1,q}.$$

Sums in these expressions are reduced to their last terms since we neglect all dissociation/recombination process except with participation of the highest excitation level.

Let us introduce new variables $X_1 = X_1^{(qe)} + \varepsilon X_1^{(0)}$, $R_1 = R_1^{(qe)} + \varepsilon R_1^{(0)}$ using the relationship $\tilde{j}'_{q-1}(X_1^{(0)})X_1^{(qe)} = \tilde{j}'_{q-1}(X_1)X_1^{(qe)}$, which follows from equations $\tilde{j}'_m(X_1^{(qe)})X_1^{(qe)} = 0$ and $\tilde{j}'_m(X+Y)Z = \tilde{j}'_m(X)Z + \tilde{j}'_m(Y)Z$. Returning to dimensional variables, one can rewrite (35) as

$$
\begin{aligned}
&(1-\delta_{q,0})\tilde{j}_{q-1}(X_1^{(qe)})X_1 - (1-\delta_{q,q_m})\tilde{j}_q(X_1^{(qe)})X_1 \\
&-\delta_{q,q_m}\left(P_{q,d}X_{1,q} - P_{q,r}n_4n_5\right) - S_1\left(X_{1,q}^{(qe)}\right)R_1 \\
&+(1-\delta_{q,0})\tilde{j}'_{q-1}(X_1)X_1^{(qe)} - (1-\delta_{q,q_m})\tilde{j}'_q(X_1)X_1^{(qe)} = 0.
\end{aligned}
\tag{36}
$$

From the expression for R_1 one can see that reaction rate is determined not by the equilibrium or quasi-equilibrium distribution, but by the quasi-stationary one, X_1, that will be found from equation (36).

Summation of these equations (analogous to that in Section 2.2), yields a set of equations

$$
\begin{aligned}
&(1-\delta_{q,q_m})\tilde{j}_q(X_1^{(qe)})X_1 + (1-\delta_{q,q_m})\tilde{j}'_q(X_1)X_1^{(qe)} \\
&+\delta_{q,q_m}\left(P_{q,d}X_{1,q} - P_{q,r}n_4n_5\right) + \sum_{k=0}^{q_m} S_1\left(X_{1,k}^{(qe)}\right)R_1 = 0.
\end{aligned}
\tag{37}
$$

This set of equations has a more complex structure than (22): it contains non-diagonal terms due to the $\tilde{j}'_q(X_1)X_1^{(qe)}$ term. To solve (37), we will use an iterative procedure similar to that suggested in [8] for a two-temperature case. Following definition from [8], [10] we consider only the case of a so called weekly exited system. This means that the populations of exited levels are so small that the VV transitions occur mainly with participation of the low levels. This can be expressed as $Q_{q+1,q}^{l,l+1}X_{1,q+1}X_{1,l} \gg Q_{q+1,q}^{q,q+1}X_{1,q+1}X_{1,q}$ while $l \ll q$. In this case $Q_{q+1,q}(X)$ is weekly dependent on the form of X as a function of q. Since VV-exchange with participation of low levels predominates, the main contribution into $Q_{q+1,q}(X)$ comes from terms with small l, for which the distribution function for which is close to Boltzmann distribution. We shall keep all this in mind and apply this procedure later, just before obtaining the expression for the reaction rate.

The expressions for the vibrational population densities formally are similar to that obtained in a linear case in Section (2). The detailed balance relations (34) are used:

$$
X_{1,q+1} = a_qX_{1,q} + \tilde{b}_q, \qquad a_q = \frac{\tilde{P}_{q,q+1}\left(X_1^{(qe)}\right)}{\tilde{P}_{q+1,q}\left(X_1^{(qe)}\right)} = \frac{\chi_{q+1}}{\chi_q},
$$

$$
\tilde{b}_q = \frac{1}{\tilde{P}_{q+1,q}\left(X_1^{(qe)}\right)}\left(\sum_{k=0}^{q} R_1S_1\left(X_{1,k}^{(qe)}\right) - \tilde{j}'_q(X_1)X_1^{(qe)}\right) \equiv \frac{R_1S_1\left(\Theta^{(q)}\right)}{\tilde{P}_{q+1,q}\left(X_1^{(qe)}\right)} + \tilde{b}'_q,
$$

$\Theta^{(q)}$ is defined in (23). This allows to use eq. (24) and to write

$$
X_{1,q+1} = \prod_{i=0}^{q} a_iX_{1,0} + \sum_{m=0}^{q}\tilde{b}_m\prod_{i=m+1}^{q} a_i. \tag{38}
$$

Thus

$$
\begin{gathered}
X_{1,q} = \frac{\chi_q}{\chi_0} X_{1,0} + R_1 \tilde{c}_q + \tilde{\tilde{c}}_q, \\
\tilde{c}_q = \sum_{m=0}^{q-1} \frac{\chi_q}{\chi_{m+1}} \frac{S_1\left(\Theta^{(m)}\right)}{\tilde{P}_{m+1,m}(X_1^{(qe)})}, \qquad \tilde{\tilde{c}}_q(X_1) = -\sum_{m=0}^{q-1} \frac{\chi_q}{\chi_{m+1}} \frac{\tilde{j}'_m(X_1) X_1^{(qe)}}{\tilde{P}_{m+1,m}(X_1^{(qe)})}.
\end{gathered}
\tag{39}
$$

As in previous section, $X_{1,0}$ can be determined from the normalization condition:

$$
n_1 = \sum_{q=0}^{q_m} X_{1,q} = \sum_{q=0}^{q_m} \frac{\chi_q}{\chi_0} X_{1,0} + R_1 \sum_{q=1}^{q_m} \tilde{c}_q + \sum_{q=1}^{q_m} \tilde{\tilde{c}}_q \equiv \frac{\tilde{Q}_1}{\chi_0} X_{1,0} + R_1 \tilde{C} + \tilde{\tilde{C}},
$$

which gives

$$
X_{1,q} = \left(\frac{\chi_q}{\tilde{Q}_1} \left(n_1 - \tilde{\tilde{C}} \right) + \tilde{\tilde{c}}_q \right) + R_1 \left(\tilde{c}_q - \frac{\chi_q}{\tilde{Q}_1} \tilde{C} \right) \equiv X^{(qe)}_{1,q} + A_q + R_1 B_q, \tag{40}
$$

where B_q is determined only by the quasi-equilibrium distribution and therefore does not change during the iterative procedure. After multiplying Eq (40) by $-P_{q,d}$ and adding $-P_{q,r} n_3 n_4$ to both sides we obtain

$$
R_1 = \frac{R^{(qe)} - P_{q_m,d} A_{q_m}}{1 + P_{q_m,d} B_{q_m}}, \qquad R^{(qe)} = P_{q_m,d} X^{(qe)}_{1,q_m} - P_{q_m,r} n_4 n_5. \tag{41}
$$

The iterative algorithm is described below.

$$
X_{1,q\,(n)} = X^{(qe)}_{1,q} + A_{q(n)} + R_{1(n)} B_q \qquad A_{q_m(n)} = A_{q_m}(X_{1(n-1)}).
$$

Using $X_1^{(qe)}$ for a primeval approximation for X_1, we have $Q_{i,j\,(0)} = Q_{i,j}(X_1^{(qe)})$, $\tilde{j}'_{q\,(0)}(X_1^{(qe)}) X_1^{(qe)} = 0$, $\tilde{\tilde{c}}_q = \tilde{\tilde{C}} = 0$. Then $A_{q\,(0)} = 0$ and $X_{1,q\,(0)} = X^{(qe)}_{1,q} + R_{1(0)} B_q$ according to (40), that coincides with the result for a small admixture (26). After substituting it into expressions for $\tilde{\tilde{c}}_q$ and $\tilde{\tilde{C}}$, one obtains

$$
R_{1\,(0)} = \frac{R^{(qe)}}{1 + P_{q_m,d} \left(B_{q_m} + A_{q_m}(\tilde{c}) \right)}. \tag{42}
$$

since $\tilde{\tilde{c}}_q(X_{1\,(0)}) = R_1 \tilde{\tilde{c}}_q(B) = R_1 \tilde{\tilde{c}}_q(\tilde{c})$, $\tilde{\tilde{C}}(B) = \tilde{\tilde{C}}(\tilde{c})$. If VV processes are negligible then $\tilde{\tilde{c}}_q \to 0$, $\tilde{\tilde{C}} \to 0$, $\tilde{c}_q \to c_q$ and $\tilde{C} \to C$. It gives us (27) obtained for small dissociating admixture concentration. In further approximations no corrections in denominator of the expression for reaction rate arise, but only in the numerator. For the first iteration we obtain the same result as for the zero one, and for the second one

$$
R_{1\,(2)} = \frac{R^{(qe)} \left(1 - \left(1 + P_{q_m,d} B_{q_m} \right)^{-1} A_{q_m}(\tilde{\tilde{c}}(\tilde{c})) \right)}{1 + P_{q_m,d} \left(B_{q_m} + A_{q_m}(\tilde{c}) \right)}.
$$

To study the dependence of the dissociation rate on pressure, let us separate the dissociation and recombination processes in expression (42)

$$R_1 = R_{1,d} - R_{1,r}, \tag{43}$$

and introduce the following dependencies, keeping $\xi_\alpha = [M]^{-1} n_\alpha$, $\alpha = 1, ..., 5$, constant:

$$\tilde{P}_{i,j} = [M] \tilde{p}_{i,j}(\xi_1, ..., \xi_5), \qquad P_{q,d} = P^{(u)}_{q,d} + [M] p^{(c)}_{q,d}(\xi_1, ..., \xi_5),$$
$$P_{q,r} = P^{(u)}_{q,r} + [M] p^{(c)}_{q,r}(\xi_1, ..., \xi_5), \quad \tilde{c}_q \approx [M]^{-1} c'_q, \quad \tilde{C} \approx [M]^{-1} \tilde{C}', \quad B_q \approx [M]^{-1} B'_q.$$

Here $\tilde{p}_{i,j} = q^{(1)}_{i,j} \xi_1 + \sum\limits_{\alpha=1}^{5} p^{(\alpha)}_{i,j} \xi_\alpha$, $p^{(c)}_{q,d} = \sum\limits_{\alpha=1}^{5} p^{(c,\,\alpha)}_{q,d} \xi_\alpha$, and $p^{(c)}_{q,r} = \sum\limits_{\alpha=1}^{5} p^{(c,\,\alpha)}_{q,r} \xi_\alpha$; $p^{(\alpha)}_{i,j}$ are responsible for VT processes, while $q^{(1)}_{i,j}$ for the VV processes; $p^{(c,\,\alpha)}_{q,d}$ are responsible for collisional dissociation processes; $p^{(c,\,\alpha)}_{q,r}$ are responsible for the three particle recombination reactions. We also use that $\tilde{\tilde{c}}_{B\,q} = [M]^{-1} \tilde{\tilde{c}}'_{B\,q}$, $\tilde{\tilde{C}}_B = [M]^{-1} \tilde{\tilde{C}}'_B$, and therefore $A_q = [M]^{-1} A'_q$. Here all primed parameters are independent of pressure. As a result, in a low pressure limit, for $R_{1,d}$ defined by (43) and (42) one obtains

$$R_{1\,(0),d\,0} = -\frac{\chi_{q_m}}{B'_{q_m} + A'_{q_m}(\tilde{c})} \xi_1 [M]^2. \tag{44}$$

In a high pressure limit it results in

$$R_{1\,(0),d\,\infty} = -\frac{p^{(c)}_{q_m,d} \chi_{q_m}}{1 + p^{(c)}_{q_m,d} \left(B'_{q_m} + A'_{q_m}(\tilde{c}) \right)} \xi_1 [M]^2. \tag{45}$$

Analogous to the case of small admixture, the low pressure reaction rate does not depend on the reaction probability, and with pressure increase we observe a transition from unimolecular reaction mechanism to the collisional one. The difference between (45) and (33) consists in that in (45) we kept only the main term of expansion, proportional to $[M]^2$, while in (33) we kept also the next term, proportional to $[M]$.

For recombination part $R_{1,r}$ in a low pressure limit one obtains

$$R_{1\,(0),r\,0} = \frac{P^{(u)}_{q_m,r} \xi_4 \xi_5}{P^{(u)}_{q_m,d} \left(B'_{q_m} + A'_{q_m}(\tilde{c}) \right)} [M]^3, \tag{46}$$

and for high pressure limit

$$R_{1\,(0),r\,\infty} = \frac{p^{(c)}_{q_m,r} \xi_4 \xi_5}{1 + p^{(c)}_{q_m,d} \left(B'_{q_m} + A'_{q_m}(\tilde{c}) \right)} [M]^3. \tag{47}$$

For both dissociation and recombination processes, increasing pressure causes a transition from unimolecular regime to the collisional one.

The dependence of rates on the noble gas concentrations is not significant, though it is more complex in comparison with the case of a small reactive admixture.

3 Exchange reactions.

Expression similar to (27) can be obtained for exchange reactions $[1]+[C] \to [B]+[D]$ if concentration of reagent $[C]$ can be assumed to be constant (for instance it is high enough not to account its vanishing during chemical reactions). In this case we set $P_{N,d} = p_C^{(c)}[M]\xi_C$ in (27), where ξ_C is the concentration of reagent C. S-operator defined by (16) should be also modified. For exchange reactions the relation between reaction rates is a little bit more complicated. These relations can be find from the set of relations (14) for different k:

$$\zeta_{1,k}R_1 + \zeta_{C,k}R_C + \zeta_{B,k}R_B + \zeta_{D,k}R_D = 0.$$

Taking three different k (or two different k if B and D are identical) we can obtain expressions $R_C = \eta_C R_1$, $R_B = \eta_B R_1$, $R_D = \eta_D R_1$, where η_C, η_B, η_D are the functions of $\zeta_{1,k}$, $\zeta_{C,k}$, $\zeta_{B,k}$, $\zeta_{D,k}$. Therefore the modified S_{ex}-operator is defined by the relation

$$\left(\frac{\partial X_{1,q}}{\partial n_1} + \eta_C\frac{\partial X_{1,q}}{\partial n_C} + \eta_B\frac{\partial X_{1,q}}{\partial n_B} + \eta_D\frac{\partial X_{1,q}}{\partial n_D}\right) R_1 \equiv S_{ex1}(X_{1,q})R_1, \tag{48}$$

and one should use $S_{ex1}(X_{1,q}^{qe})$ instead of S for calculation c_{q_m} and C in Eq.(27). This leads to the modification of the pressure dependence of the reaction rate

$$R_1 = -\frac{p_C^{(c)}\chi_{q_m}Q_1^{-1}\xi_C\xi_1}{1 + p_C^{(c)}\xi_C\left[c'_{q_m} - C'\chi_{q_m}Q_1^{-1}\right]}[M]^2. \tag{49}$$

In this expression the denominator is independent of pressure. Thus, in contrast to the case of unimolecular reactions, the reaction order does not change with pressure and reaction rate differs from the equilibrium one at all pressures. The last feature can be interpreted in the same way as the previous result for the dissociation reactions (see equations (32, 33)): the high-pressure limit does not imply vanishing the ratio of reaction time to relaxation time, unlike in unimolecular reactions:

$$p_C^{(c)}\xi_C\left[c'_{q_m} - C'\chi_{q_m}Q_1^{-1}\right] \approx \frac{p_C^{(c)}\xi_C}{p_{q_m,q_m-1}} \approx \frac{\tau_{VT}Q_1}{\tau_{chem}\chi_{q_m}} = \varepsilon\frac{Q_1}{\chi_{q_m}},$$

$$R_1 \approx -\frac{p_C^{(c)}\chi_{q_m}\xi_C\xi_1 p_{q_m,q_m-1}}{p_C^{(c)}\xi_C Q_1}[M]^2 = \frac{\chi_{q_m}p_{q_m,q_m-1}\xi_1}{Q_1}[M]^2.$$

4 Parallel Reactions.

4.1 Dissociation into different channels from one vibrational state.

Let us first consider the simplest example of parallel reactions, where a molecule of sort 1 decays from vibrational level q_m in two channels C and D, that can be described as $1 \rightarrow C_1 + C_2$ and $1 \rightarrow D_1 + D_2$ respectively. Only one sort of noble gas with concentration ξ_2 is considered. This situation can be described by setting in the previously obtained formulas for reaction rates

$$P_d = P_C + P_D, \qquad P_I = P_I^{(u)} + p_I^{(c)}\xi_2[M], \qquad I = C, D.$$

From (14) it follows that

$$R_{C_1} = R_{C_2} = R_{D_1} = R_{D_2} = -R_1.$$

Then the S-operator can be written as

$$S_1(X_{1,q}) = \left(\frac{\partial}{\partial n_1} - \frac{\partial}{\partial n_{C_1}} - \frac{\partial}{\partial n_{C_2}} - \frac{\partial}{\partial n_{D_1}} - \frac{\partial}{\partial n_{D_2}}\right) X_{1,q}.$$

Then the level population

$$X_{1,q} = n_1 \frac{\chi_q}{Q_1} + R_1 A_q, \qquad A_q = c_q - C\frac{\chi_q}{Q_1},$$

where c_n and C contains S_1-factor as a co-factor. As a result for total dissociation rate $R_1 = -P_{q_m,d} X_{1,q_m} = -P_{q_m,d} n_1 \chi_{q_m}/Q_1 - P_{q_m,d} R_1 A_{q_m}$ we obtain:

$$R_1 = -\frac{P_{q_m,d} n_1 \chi_{q_m}/Q_1}{1 + P_{q_m,d} A_{q_m}} = -\frac{(P_C + P_D)\, n_1 \chi_{q_m}}{Q_1\left[1 + (P_C + P_D)\, A_{q_m}\right]} = R_{1C} + R_{1D},$$

$$R_{1I} = -\frac{\left(P_I^{(u)} + p_I^{(c)}\xi_2[M]\right)\chi_{q_m}\xi_1}{Q_1\left[1 + \left(\left(P_C^{(u)} + P_D^{(u)}\right)[M]^{-1} + p_C^{(c)} + p_D^{(c)}\right) A'_{q_m}\right]}[M], \tag{50}$$

where $A_q = A'_q[M]^{-1}$, and A'_q is independent of pressure.

From (50) we see that reactions C and D depend on each other since the rates R_I depend on P_C and P_D. Therefore a traditional concept of rate constants can not be used.

This effect can be observed experimentally if only one of the channels can be excluded, for instance if reaction C is caused by some additional component C.

4.2 Parallel reactions of one species in different vibrational states.

One more example of non-equilibrium effects in parallel reactions can be illustrated by considering the situation when a molecule of sort 1 on level K reacting with a molecule of sort C. We further denote this reaction as reaction C, while reaction of the molecule on level N we denote as reaction D. The activation energy of reaction C is lower than D. Now let us assume that the perturbation of the C-component distribution function as well as concentrations of the products are negligible. It can be described by substituting $P_{n,d}$ into equation (17) by $P_C\delta_{q,K} + P_D\delta_{q,q_m}$. The term that contains the derivations over number densities of species $\sum\limits_\alpha \frac{\partial X_1^{(qe)}}{\partial n_\alpha} R_\alpha$ can not be reduced to the S-factor due to the lack of relations that reflects the elements conservation (14). Remembering eq. (28), this sum can be written as

$$\sum_\alpha \frac{\partial X_{1,k}^{(qe)}}{\partial n_\alpha} R_\alpha = \sum_\alpha \frac{X_{1,k}^{(qe)}}{n_1} \left(\delta_{1\alpha} + \frac{n_1\left(e_1^{(V)}(k) - E^{(V)}\right)}{kT} \frac{\partial \ln(kT)}{\partial n_\alpha} \right) R_\alpha .$$

Assuming thermal effects to be small, we shall further neglect the derivation $\partial T/\partial n_\alpha$. Then the set of equations (22) for $X_{1,q} = X_{1,q}^{(qe)} + X_{1,q}^{(0)}$ can be rewritten as

$$j_q(X) - P_C X_{1,K}\theta(q-K) - \sum_{k=0}^{q} R X_{1,k}^{(qe)}/n_1 = 0, \qquad q = 0, ..., q_m - 1,$$

where j_q is defined in (17) and equation (21) is replaced by

$$R = -P_C X_{1,K} - P_D X_{1,q_m} = R_C + R_D. \tag{51}$$

Here $\theta(x)$ is the Heaviside function: $\theta = 0$ for $x < 0$ and $\theta = 1$ for $x \geq 0$. The recurrent relationship thus takes the form

$$X_{1,q+1} = \frac{\chi_{q+1}}{\chi_q} X_{1,q} + \frac{1}{P_{q+1,q}} \left[R \sum_{k=0}^{q} \frac{X_{1,k}^{(qe)}}{n_1} + P_C X_{1,K}\theta(q-K) \right].$$

Solution of this equation can be written in the form (23) where b_q should be replaced by b'_q

$$b'_q = b_q + \frac{P_C}{P_{q+1,q}} X_{1,K}\theta(q-K) = \frac{R}{P_{q+1,q}} \frac{\Theta^{(q)}}{n_1} + \frac{P_C}{P_{q+1,q}} X_{1,K}\theta(q-K).$$

After some algebra, similar to that done in the previous section, for the vibrational population distribution one obtains

$$X_{1,q} = \chi_q X_{1,0}/\chi_0 + \theta(q-1-K) P_C X_{1,K} d_q + R c_q,$$

$$d_q = \sum_{m=K}^{q-1} \frac{\chi_q}{\chi_{m+1}} \frac{1}{P_{m+1,m}},$$

$d_q = 0$ when $q \le K$, and c_q is defined in (25).

Taking into account that $X_{1,K} = \chi_K X_{1,0}/\chi_0 + Rc_K$, expression for $X_{1,q}$ can be rewritten as

$$X_{1,q} = \left[\chi_q + \theta(q-1-K)P_C\chi_K d_q\right]\frac{X_{1,0}}{\chi_0} + R\left[c_q + \theta(q-1-K)P_C c_K d_q\right]. \qquad (52)$$

As shown further, due to depletion of level K caused by corresponding chemical reaction, this distribution function can vanish at some level $q_0 \le q_m$. In this case the level population for $q > q_0$ becomes negative and therefore has no physical meaning (as for $q > q_m$) and we should reformulate the normalization condition for $X_{1,0}$

$$n_1 = \sum_{q=0}^{q_0} X_{1,q} = \frac{X_{1,0}}{\chi_0}\left[\sum_{q=0}^{q_0}\chi_q + P_C\chi_K\sum_{q=0}^{q_0}\theta(q-1-K)d_q\right]$$

$$+R\sum_{q=0}^{q_0} c_q + RP_C c_K\sum_{q=0}^{q_0}\theta(q-1-K)d_n$$

$$= X_{1,0}\left(Q_{1\,0} + H_0\right)/\chi_0 + R\left(C_0 + G_0\right),$$

$$C_0 = \sum_{q=0}^{q_0} c_q, \qquad G_0 = P_C c_K\sum_{q=0}^{q_0}\theta(q-1-K)d_q = P_C c_K\sum_{q=K+1}^{q_0} d_q = P_C c_K D_0,$$

$$Q_{1\,0} = \sum_{q=0}^{q_0}\chi_q, \qquad H_0 = P_C\chi_K\sum_{q=0}^{q_0}\theta(q-1-K)d_q = P_C\chi_K\sum_{q=K+1}^{q_0} d_q = P_C\chi_K D_0.$$

$X_q^{(qe)}$ is then redefined as $X_q^{(qe)} = n_1\chi_q/Q_{1\,0}$.

If q_0 is larger than q_m, then q_m should be used instead of q_0 and $Q_{1\,0}$, C_0, G_0, H_0 should be replaced by Q_1, C, G, H defined in Section 2.2.

As a result we obtain

$$X_{1,0} = (Q_{1\,0} + H_0)^{-1}(n_1 - R(C_0 + G_0))\chi_0,$$

and thus

$$X_{1,q} = \frac{Q_{1\,0}}{Q_{1\,0} + H_0}\left[X_{1,q}^{(qe)} + \theta_q P_C X_{1,K}^{(qe)} d_q\right]$$

$$+R\left[c_q - Q_{1\,0}\frac{C_0 + G_0}{Q_{1\,0} + H_0}\frac{X_{1,q}^{(qe)}}{n_1} + \theta_q P_C d_q\left(c_K - Q_{1\,0}\frac{C_0 + G_0}{Q_{1\,0} + H_0}\frac{X_{1,K}^{(qe)}}{n_1}\right)\right] \qquad (53)$$

$$= n_1(Q_{1\,0} + H_0)^{-1}\left[\chi_q + \theta_q P_C\chi_K d_q\right] + R\left[W_q + \theta_q P_C d_q W_K\right].$$

Here and further $\theta_q \equiv \theta(q-1-K)$ and $W_q = c_q - \dfrac{C_0+G_0}{Q_{1\,0}+H_0}\chi_q$. This expression coincides with (26) when $P_C \to 0$ and $q_0 \to q_m$.

For the first term in (51) one has

$$R_C = -P_C X_{1,K} = -(Q_{1\,0}+H_0)^{-1} P_C \chi_K n_1 - R P_C W_K, \tag{54}$$

and for the second one

$$R_D = -P_D X_{q_0} = -\frac{P_D\left(\chi_{q_0} + P_C \chi_K d_{q_0}\right) n_1}{(Q_{1\,0}+H_0)} - R P_D\left(W_{q_0} + P_C d_{q_0} W_K\right). \tag{55}$$

It means that reaction D is treated as a reaction from the highest (floating) populated level, but not necessarily from level q_m. If the dissociation from every level $q \le q_0$ is considered, then more smooth dependence of reaction rates on a floating level q_0 will be obtained, but it leads to more complex formulas that we were trying to avoid for the clarity of presentation. If dissociation is selective, occurring from level q_m only, the simplifications in all further results can be obtained by setting $P_D = 0$.

Then for reaction rate (51) one has

$$R = -n_1 \frac{P_C \chi_K (1 + P_D d_{q_0}) + P_D \chi_{q_0}}{Q_{1\,0} S_0},$$

$$S_0 = 1 + P_D\left(c_{q_0} - C_0 Q_{1\,0}^{-1} \chi_{q_0}\right) + Q_{1\,0}^{-1} D_0 P_C \chi_K \tag{56}$$

$$+P_C\left((1+P_D d_{q_0})\left(c_K - C_0 Q_{1\,0}^{-1}\chi_K\right) + Q_{1\,0}^{-1} D_0 P_D\left(c_{q_0}\chi_K - c_K \chi_{q_0}\right)\right).$$

In the limit $P_C \to 0$ this expression converts into (27), since q_0 should be replaced by q_m in this case.

After substituting (56) into (53) and some algebra one obtains for the quasi-stationary distribution function

$$X_{1,q} = \frac{n_1}{Q_{1\,0} S_0}\left[\chi_q - P_C c_K(\theta_q \chi_K - \chi_q) - P_C \chi_K \left((1-\theta_q)c_q - \theta_q \hat{d}_q\right) + \varphi_{0\,q}\right],$$

$$\hat{d}_q = \sum_{m=K}^{q-1} \frac{\chi_q}{\chi_{m+1}} \frac{1}{P_{m+1,m}} \left(1 - S\left(\theta^{(m)}\right)\right), \tag{57}$$

$$\varphi_{0\,q} = P_C P_D\left(\chi_K(\theta_q d_n c_{q_0} - d_{q_0} c_n)\right.$$

$$\left.+ c_K(d_{q_0}\chi_q - \theta_q d_q \chi_{q_0})\right) + P_D(c_{q_0}\chi_q - c_q \chi_{q_0}).$$

The first term in $\varphi_{0\,q}$ proportional to $P_C P_D$ can be treated as a continuous function of q in the interval $K < q \le N_0$. It decreases when q increases and vanishes at $q = q_0$, therefore it is positive. The same is for $0 \le q \le K$ since it vanishes at $q = K$. The second term is positive for all $q < q_0$. The condition for determination q_0 is $X_{1,q_0} = 0$. This leads to the equation ($\varphi_{0\,q_0} = 0$)

$$(1 + P_C c_K)\chi_{q_0^0} - P_C \chi_K (c_K - \hat{d}_{q_0^0}) = 0. \tag{58}$$

q_0^0 being the solution of this equation may be non-integer. Then the nearest integer less than q_0^0 should be chosen for q_0.

Considering P_C as a function of the mixture number density $[M]$ in the form $P_C = P_C^{(u)} + p_C^{(c)}\xi_C[M]$ one gets the expression for q_0^0 as a function of $[M]$:

$$\frac{\chi_{q_0^0}}{\chi_K} = \frac{\left(P_C^{(u)} + p_C^{(c)}\xi_C[M]\right)(c'_K - \hat{d}'_{q_0^0})}{[M] + (P_C^{(u)} + p_C^{(c)}\xi_C[M])c'_K}, \tag{59}$$

where $c_i \approx c'_i[M]^{-1}$, $\hat{d}_j \approx \hat{d}'_j[M]^{-1}$ and c'_i and $\hat{d}'_j$ are independent of $[M]$. When $\hat{d}_{q_0}$ is much smaller than c_K, this equation can be solved by iterations.

Since the behavior of the system differs significantly for the case of $q_0^0 < q_m$ and $q_0^0 > q_m$, we separate them in our analysis. Introducing critical value of the mixture number density

$$[M]_c = \frac{P_C^{(u)}(\chi_{q_m}^{-1}\chi_K(c'_K - \hat{d}'_{q_0^0}) - c'_K)}{1 + p_C^{(c)}\xi_C \chi_{q_m}^{-1}\chi_K \hat{d}'_{q_0^0} - p_C^{(c)} c'_K \xi_C(\chi_{q_m}^{-1}\chi_K - 1)} = \frac{P_C^{(u)} c'_K}{\varepsilon_c^{(c)} - p_C^{(c)}\xi_C c'_K},$$

$$\varepsilon_c^{(c)} = \frac{1}{\chi_{q_m}^{-1}\chi_K - 1 - \chi_{q_m}^{-1}\chi_K \hat{d}'_{q_0^0} c'^{-1}_K}, \tag{60}$$

and using relations (58) and (59)($q_0^0 < q_m$ corresponds to $\chi_{N_0^0} > \chi_N$ and therefore to $\left(\varepsilon_c^{(c)} - p_C^{(c)}\xi_C c'_K\right)([M] - [M]_c) < 0$) one can conclude that if $p_C^{(c)}\xi_C c'_K > \varepsilon_c^{(c)}$ then

$[M]_c < 0$ and thus $q_0^0 < q_m$ at any values of $[M]$, and q_0^0 is determined according to (59). If $p_C^{(c)} \xi_C c'_K < \varepsilon_c^{(c)}$, then $q_0^0 < q_m$ at $[M] < [M]_c$. If $[M] > [M]_c$ then $q_0^0 > q_m$ and in all expressions q_0^0 should be replaced by q_m and we shall use notations C, D and Q_1 instead of C_0, D_0 and $Q_{1\,0}$ respectively.

From expression (59) it is seen that for the high-pressure limit (that implies $[M] > [M]_c$)

$$\frac{\chi_{q_0^0}}{\chi_K} = \frac{p_C^{(c)} \xi_C (c'_K - \hat{d}'_{q0^0})}{1 + p_C^{(c)} \xi_C c'_K}. \tag{61}$$

Since the RHS of this relation is always less than unity, the solution for $q_0^0 \geq K$ always exist. If $p_C^{(c)} \xi_C c'_K \leq \varepsilon_c^{(c)}$, then $q_0^0 \geq q_m$ and in all expressions q_0 should be replaced by q_m. If $p_C^{(c)} \xi_C c'_K \leq \varepsilon_c^{(c)}$, q_0 is determined by expression (61).

For the low-pressure limit one obtains

$$\frac{\chi_{q_0^0}}{\chi_K} = 1 - \frac{\hat{d}'_{q_0^0}}{c'_K}, \tag{62}$$

then for $\hat{d}'_{q_0^0} \ll c'_K$ the maximal level q_0 is close to K.

4.3 Parallel reaction rates.

Let us consider expression (51), in order to separate the contribution of reaction C from that of reaction D and to study their mutual impact, using expressions (54), (55) for R_C and R_D and expressions

$$\begin{gathered}
X_{1,K} = \frac{X_K^{(qe)}}{S_0} \left[1 + P_D c_{q_0} \left(1 - \frac{\chi_{q_0}}{\chi_K} \frac{c_K}{c_{q_0}} \right) \right], \\
X_{1,q_0} = \frac{X_{q_0}^{(qe)}}{S_0} \left[1 + P_C c_K \left(1 - \frac{\chi_K}{\chi_{q_0}} \left(1 - \frac{\hat{d}_{q_0}}{c_K} \right) \right) \right].
\end{gathered} \tag{63}$$

Since for rather high q_0 values X_{1,q_0} slightly depends on q_0, one can replace it by q_0^0 and rewrite the expression for X_{1,q_0} as

$$X_{1,q_0} \approx \frac{X_{q_0}^{(qe)}}{S_0} \frac{\left(\varepsilon_c^{(c)} - p_C^{(c)} \xi_C c'_K \right)}{\varepsilon_c^{(c)} [M]} \left([M] - [M]_c \right). \tag{64}$$

Thus X_{1,q_0} vanishes when q_0 becomes smaller than q_m.

Introducing the partial rates $R_C^0 = R_C(P_D = 0)$ and $R_D^0 = R_D(P_C = 0)$ that correspond to the reactions without parallel ones, $R_C = P_C X_{1,K}$ and $R_D = P_D X_{1,q_0}$

rates for C and D reactions respectively can be represented as

$$R_C = R_C^0 \Delta_C, \qquad R_C^0 = -P_C \frac{n_1}{Q_{1\,0} S_{C0}} \chi_K,$$

$$\Delta_C = \frac{S_{C0}}{S_0} \left(1 + P_D(c_{q_0} - c_K \chi_K^{-1} \chi_{q_0})\right), \tag{65}$$

$$S_{C0} = 1 + P_C \left(c_K - Q_{1\,0}^{-1}(C_0 - D_0)\chi_K\right),$$

$$R_D = R_D^0 \Delta_D, \qquad R_D^0 = -P_D \frac{n_1}{Q_{1\,0} S_{D0}} \chi_{q_0},$$

$$\Delta_D = \frac{S_{D0}}{S_0} \left(1 + P_C c_K - P_C \chi_{q_0}^{-1} \chi_K (c_K - \hat{d}_{q_0})\right), \tag{66}$$

$$S_{D0} = 1 + P_D \left(c_{q_0} - C_0 Q_{1\,0}^{-1} \chi_{q_0}\right).$$

Factors Δ_{C0} and Δ_{D0} describe the mutual effect of parallel reactions. Their deviation from unity indicates the scope of the effect. If $q_0 \geq q_m$ then the rate R_{D0}^0 coincides with R in (27).

If $q_0 \leq q_m$ then the expression for Δ_D can be rewritten using the relationship (58)

$$\Delta_D = \frac{S_{D0}}{S_0}(1 + P_C c_K) \left(1 - \frac{\chi_{q_0^0}}{\chi_{q_0}} \frac{c_K - \hat{d}_{q_0}}{c_K - \hat{d}_{q_0^0}}\right) \tag{67}$$

Since q_0^0 and q_0 are very close to each other, Δ_D in (67) is very close to zero. This means blocking reaction D for $q_0 \leq q_m$.

From (63) and (66) one can see that X_{1,q_m} and Δ_D become negative in the same conditions. It means that for $p_C^{(c)} \xi_C c'_K \geq \varepsilon_c^{(c)}$ reaction D is blocked regardless of pressure. For $p_C^{(c)} \xi_C c'_K < \varepsilon_c^{(c)}$ reaction D is blocked for low pressure, when $[M] < [M]_c$. In Fig.1 domains on $[M] - p_C^{(c)\prime}$ plane where reaction D is allowed or blocked are shown ($p_C^{(c)\prime} = p_C^{(c)} \xi_C c'_K / \varepsilon_c^{(c)}$).

From expressions (65), (66) the asymmetry of reactions C and D can be seen, since Δ_D vanishes under described conditions. It is also shown by the fact that $[M]_c$ and $\varepsilon_c^{(c)}$ depend only on probabilities of reaction C. It should be also mentioned that both $\varepsilon_c^{(c)}$ and $[M]_c$ are pressure independent.

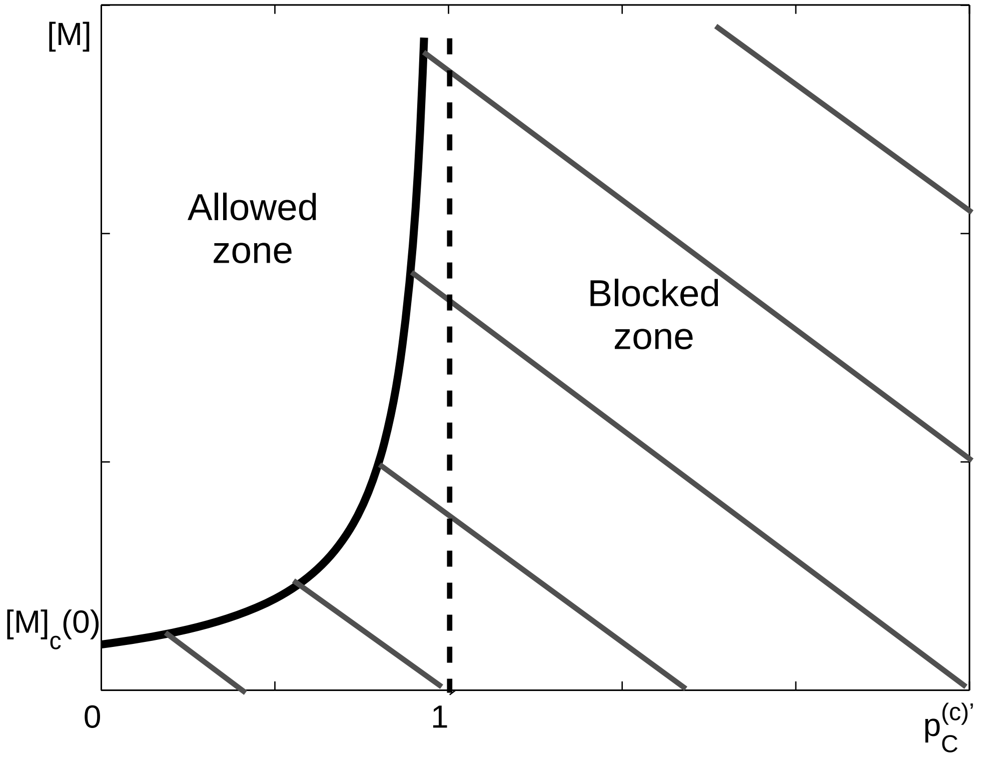

Figure 1. Domains on $[M] - p_C^{(c)\prime}$ plane where reaction D is allowed and blocked; $p_C^{(c)\prime} = p_C^{(c)}\xi_C c_K'/\varepsilon_c^{(c)}$. The curve distinguishing these domains is a function $[M]_c = [M]_c(p_C^{(c)\prime})$ (see eq.(60)); $[M]_c(0) = P_C^{(u)}c_K'/\varepsilon_c^{(c)}$. For $P_C^{(u)} = 0$ allowed/blocked domains degenerate to $p_C^{(c)\prime} < 1$ and to $p_C^{(c)\prime} > 1$ ones respectively.

4.4 Dependence of reaction rates on pressure.

Now let us analyze the behavior of these expressions at low and high pressure limits assuming component concentrations $\xi_\alpha = n_\alpha/[M]$, $\alpha = 1, 2, C$ to be fixed. Further, opposite to (33), we keep only the principal terms in the correspondent expansions over $[M]$.

The following cases exist:

I. $P_C = P_C^{(u)} + P_C^{(c)} = P_C^{(u)} + p_C^{(c)}\xi_C[M]$, $P_D = P_D^{(u)} + P_D^{(c)} = P_D^{(u)} + p_D^{(c)}\xi_2[M]$;

II. $P_C = P_C^{(c)} = p_C^{(c)}\xi_C[M]$, $P_D = P_D^{(u)} + P_D^{(c)} = P_D^{(u)} + p_D^{(c)}\xi_2[M]$;

III. $P_C = P_C^{(u)} + P_C^{(c)} = P_C^{(u)} + p_C^{(c)}\xi_C[M]$, $P_D = P_D^{(c)} = p_D^{(c)}\xi_2[M]$;

IV. $P_C = P_C^{(u)}$, $P_D = P_D^{(u)} + P_D^{(c)} = P_D^{(u)} + p_D^{(c)}\xi_2[M]$;

V. $P_C = P_C^{(u)} + P_C^{(c)} = P_C^{(u)} + p_C^{(c)}\xi_C[M]$, $P_D = P_D^{(u)}$;

VI. $P_C = P_C^{(c)} = p_C^{(c)}\xi_C[M]$, $P_D = P_D^{(c)} = p_D^{(c)}\xi_2[M]$;

VII. $P_C = P_C^{(c)} = p_C^{(c)}\xi_C[M]$, $P_D = P_D^{(u)}$;

VIII. $P_C = P_C^{(u)} = P_C^{(u)}$, $P_D = P_D^{(c)} = p_D^{(c)}\xi_2[M]$;

IX. $P_C = P_C^{(u)}$, $P_D = P_D^{(u)}$.

Case I is the case with two dissociation reactions from level K and N_0 respectively, running in unimolecular and collisional channels. Cases II and III have one reaction with molecules on one of the levels and dissociation from another level. Cases IV and V represent dissociation from both levels K and g_0, and one of the reactions is purely unimolecular. Case IV has two chemical reactions of the molecules on levels K and g_0 and components C and 2 respectively. Analogous are the cases VII and VIII. Representative of case IX can be two reactions of isomerization.

Here considering high pressure limit we assume that $[M] > [M]_c$. For low pressure limit we assume that $[M] < [M]_c$ if $[M]_c$ is defined and nonzero.

Let us start with case I. We use the following expressions

$$
\begin{gathered}
c_g \approx c'_g[M]^{-1}, \qquad C_0 \approx C'_0[M]^{-1}, \\
d_g = d'_g[M]^{-1}, \qquad \hat{d}_{gm} \approx \hat{d}'_{gm}[M]^{-1}, \qquad D_0 = D'_0[M]^{-1}.
\end{gathered}
\tag{68}
$$

Corresponding limits for $R_{C,D}$ can be obtained if in expressions (65), (66) we set $P_C = P_C^{(u)} + p_C^{(c)}\xi_C[M]$, $P_D = P_D^{(u)} + p_D^{(c)}\xi_2[M]$. Then for the low pressure limit one obtains

$$
\begin{gathered}
R^0_{I\,C0} = -\frac{\xi_1\chi_K}{Q_{1\,0}c'_K - (C'_0 - D'_0)\chi_K}[M]^2, \\
\Delta_{I\,C0} = \frac{(c'_K - Q^{-1}_{1\,0}(C'_0 - D'_0)\chi_K)(c'_{g_0} - c'_K\chi^{-1}_K\chi_{g_0})}{d'_{g_0}(c'_K - C'_0Q^{-1}_{1\,0}\chi_K) + Q^{-1}_{1\,0}D'_0(c'_{g_0}\chi_K - c'_K\chi_{g_0})},
\end{gathered}
\tag{69}
$$

For $[M] < [M]_c$ factor $\Delta_{I\,D0}$ vanishes and thus reaction D is blocked.

For the high pressure limit the partial reaction rates and Δ-factors behave as follows

$$\begin{gathered}
R^0_{I\,C\infty} = -\frac{\xi_1 p_C^{(c)} \xi_C \chi_K}{Q_{1\,0}\left(1 + p_C^{(c)} \xi_C \left(c'_K - Q_{1\,0}^{-1}(C'_0 - D'_0)\chi_K\right)\right)}[M]^2, \\
\Delta_{I\,C\infty} = S^{-1}_{0\,I\,\infty}\left(1 + p_C^{(c)} \xi_C \left(c'_K - \left(C'_0 - D'_0\right) Q_{1\,0}^{-1}\chi_K\right)\right) \\
\times \left(1 + p_D^{(c)} \xi_2 \left(c'_{g_0} - c'_K \chi_K^{-1} \chi_{g_0}\right)\right), \\
S_{0\,I\,\infty} = 1 + p_D^{(c)} \xi_2 \left(c'_{g_0} - \frac{C'_0 \chi_{g_0}}{Q_{1\,0}}\right) + p_C^{(c)} \xi_C \left(\left(1 + p_D^{(c)} \xi_2 d'_{g_0}\right)\left(c'_K - \frac{C'_0 \chi_K}{Q_{1\,0}}\right)\right. \\
\left. + \frac{D'_0}{Q_{1\,0}}\left(p_D^{(c)} \xi_2 \left(c'_{g_0}\chi_K - c'_K \chi_{g_0}\right) + \chi_K\right)\right),
\end{gathered} \tag{70}$$

$$\begin{gathered}
R^0_{I\,D\infty} = -\frac{\xi_1 p_D^{(c)} \xi_2 \chi_{g_m}}{Q_1\left(1 + p_D^{(c)} \xi_2 (c'_{g_m} - C' Q_1^{-1} \chi_{g_m})\right)}[M]^2, \\
\Delta_{I\,D\infty} = \frac{1}{\varepsilon_c^{(c)} S_{I\,\infty}}\left(1 + p_D^{(c)} \xi_2 \left(c'_{g_m} - \frac{C' \chi_{g_m}}{Q_1}\right)\right)\left(\varepsilon_c^{(c)} - p_C^{(c)} \xi_C c'_K\right),
\end{gathered} \tag{71}$$

where $S_{I\,\infty}$ is the same as $S_{0\,I\,\infty}$ in (70), but with all parameters without subindex 0. Thus at high pressures and when $p_C^{(c)} \xi_C c'_K > \varepsilon_c^{(c)}$ reaction D is blocked, while if $p_C^{(c)} \xi_C c'_K < \varepsilon_c^{(c)}$ factor $\Delta_{I\,D\infty}$ has finite and nonzero limit. In the latter case subindex 0 should be also discarded in formulas (70).

Now we consider the case when only the collisional path for the reaction C is allowed, that is the case II. The results are obtained by substituting $P_C = P_C^{(c)} = p_C^{(c)} \xi_C [M]$ and $P_D = P_D^{(u)} + P_D^{(c)} = P_D^{(u)} + p_D^{(c)} \xi_2 [M]$ into expressions (65), (66). Using the relationships (68) for low pressure we have

$$\begin{gathered}
R^0_{II\,C0} = R^0_{I\,C\infty}, \\
\Delta_{II\,C0} = S^{-1}_{0\,II\,0}\Big(1 + p_C^{(c)} \xi_C (c'_K - Q_{1\,0}^{-1}(C'_0 - D'_0)\chi_K)\Big)\left(c'_{g_0} - c'_K \chi_K^{-1} \chi_{g_0}\right), \\
S_{0\,II\,0} = p_C^{(c)} \xi_C \left(d'_{g_0}\left(c'_K - Q_{1\,0}^{-1} C'_0 \chi_K\right) + Q_{1\,0}^{-1} D'_0 \left(c'_{g_0}\chi_K - c'_K \chi_{g_0}\right)\right) \\
+ c'_{g_0} - Q_{1\,0}^{-1} C' \chi_{g_0},
\end{gathered} \tag{72}$$

For $p_C^{(c)} \xi_C c'_K \geq \varepsilon_c^{(c)}$ the reaction D is blocked, as previously, while for the opposite case one should use the following expression

$$R^0_{II\,D0} = -\frac{\xi_1 \chi_{g_m} [M]^2}{Q_1 c'_{g_m} - C' \chi_{g_m}},$$

$$\Delta_{II\,D0} = S^{-1}_{II\,0} \left(c'_{g_m} - \frac{C' \chi_{g_m}}{Q_1} \right) \left(1 - \frac{p^{(c)}_C \xi_C c'_K}{\varepsilon^{(c)}_C} \right), \tag{73}$$

and replace g_0 by g_m in other expressions. $S_{II\,0}$ is the same as $S_{0\,II\,0}$ in (72), but with all parameters without subindex 0.

For high pressure we obtain the same results as in case I.

$$R^0_{II\,C\infty} = R^0_{I\,C\infty}, \quad \Delta_{II\,C\infty} = \Delta_{I\,C\infty}, \quad R^0_{II\,D\infty} = R^0_{I\,D\infty}, \quad \Delta_{II\,D\infty} = \Delta_{I\,D\infty}. \tag{74}$$

It is seen that when $P^{(u)}_C = 0$, the partial reaction rate $R^0_{II\,C}$ has the same structure in the whole range of pressures. It should be also mentioned that depending on the intensity of the collisional part of reaction C, factor $\Delta_{II\,D\infty}$ behaves differently, as in case I.

In the opposite case with $P^{(u)}_D = 0$ at low pressure limit we obtain

$$R^0_{III\,C0} = R^0_{I\,C0},$$

$$\Delta_{III\,C0} = \frac{(c'_K - Q^{-1}_{1\,0}(C'_0 - D'_0)\chi_K) \left(1 + p^{(c)}_D \xi_2 (c'_{g_0} - c'_K \chi^{-1}_K \chi_{g0}) \right)}{d'_{g_0}(c'_K - C'_0 Q^{-1}_{1\,0} \chi_K) + Q^{-1}_{1\,0} D'_0 (c'_{g_0} \chi_K - c'_K \chi_{g_0})}, \tag{75}$$

and reaction D is blocked. For high pressure it is as in case I:

$$R^0_{III\,C\infty} = R^0_{I\,C\infty}, \;\; \Delta_{III\,C\infty} = \Delta_{I\,C\infty}, \;\; R^0_{III\,D\infty} = R^0_{I\,D\infty}, \;\; \Delta_{III\,D\infty} = \Delta_{I\,D\infty}, \tag{76}$$

and again for $\Delta_{III\,D\infty}$ there are two cases depending on $p^{(c)}_C$ value.

Now let us remove the collisional paths of the reactions, starting with the case IV, when $P^{(c)}_C = 0$. For the low pressure limit we have the same results as in case I:

$$R^0_{IV\,C0} = R^0_{I\,C0}, \qquad \Delta_{IV\,C0} = \Delta_{I\,C0}, \tag{77}$$

with reaction D blocked. It is explained by the fact that at low pressure the collisional mechanism is negligible.

At the high pressure limit one obtains

$$R^0_{IV\,C\infty} = -P_C^{(u)}\frac{\xi_1\chi_K}{Q_1}[M], \qquad \Delta_{IV\,C\infty} = \frac{1+p_D^{(c)}\xi_2\left(c'_{g_m} - c'_K\chi_K^{-1}\chi_{g_m}\right)}{1+p_D^{(c)}\xi_2\left(c'_{g_m} - C'Q_1^{-1}\chi_{g_m}\right)},$$

$$R^0_{IV\,D\infty} = R^0_{I\,D\infty}, \qquad \Delta_{IV\,D\infty} = 1. \tag{78}$$

If the collisional path of reaction D is closed ($P_D^{(c)} = 0$), then for low pressures the picture is the same as in case I:

$$R^0_{V\,C0} = R^0_{I\,C0}, \qquad \Delta_{V\,C0} = \Delta_{I\,C0}, \tag{79}$$

with reaction D blocked, while for high pressure one obtains

$$R^0_{V\,C\infty} = R^0_{I\,C\infty}, \qquad \Delta_{V\,C\infty} = 1, \tag{80}$$

and reaction D is open only for $p_C^{(c)}\xi_C c'_K < \varepsilon_c^{(c)}$:

$$R^0_{V\,D\infty} = -P_D^{(u)}\frac{\xi_1\chi_{g_m}}{Q_1}[M],$$

$$\Delta_{V\,D\infty} = \Delta_{I\,D\infty}\big|_{P_D^{(c)}=0} = \frac{1 - p_C^{(c)}\xi_C\varepsilon_c^{(c)-1}}{1+p_C^{(c)}\xi_C\left(c'_K - Q_1^{-1}\left(C'-D'\right)\chi_K\right)}, \tag{81}$$

and g_0 should be replaced by g_m in expressions for reaction C.

Now let us turn to case VI with only collisional reactions ($P_C^{(u)} = P_D^{(u)} = 0$). For the partial reaction rates and Δ-factors one obtains

$$R^0_{VI\,C0} = R^0_{VI\,C\infty} = R^0_{I\,C\infty}, \qquad \Delta_{VI\,C0} = \Delta_{VI\,C\infty} = \Delta_{I\,C\infty},$$

$$R^0_{VI\,D0} = R^0_{VI\,D\infty} = R^0_{I\,D\infty}, \qquad \Delta_{VI\,D0} = \Delta_{VI\,D\infty} = \Delta_{I\,D\infty}. \tag{82}$$

In this case, one has just has one expression for all these parameters in a complete pressure range.

Case VII where $P_C^{(u)} = P_D^{(c)} = 0$, is similar to case II at low pressures:

$$R^0_{VII\,C0} = R^0_{II\,C0}, \quad \Delta_{VII\,C0} = \Delta_{II\,C0}, \quad R^0_{VII\,D0} = R^0_{II\,D0}, \quad \Delta_{VII\,D0} = \Delta_{II\,D0}. \tag{83}$$

For high pressure, one obtains

$$R^0_{VII\,C0\infty} = R^0_{I\,C\infty}, \quad \Delta_{VII\,C\infty} = 1, \quad R^0_{VII\,D\infty} = R^0_{V\,D\infty}, \quad \Delta_{VII\,D\infty} = \Delta_{V\,D\infty}. \tag{84}$$

For the opposite case, when $P_C^{(c)} = P_D^{(u)} = 0$, for low pressures and $[M] < [M]_c$ reaction D is blocked and we have

$$\begin{gathered} R^0_{VIII\,C0} = R^0_{I\,C0}, \\ \Delta_{VIII\,C0} = \frac{\left(c'_K - Q_{1\,0}^{-1}(C'_0 - D'_0)\chi_K\right)\left(1 + p_D^{(c)}\xi_2\left(c'_{g_0} - c'_K\chi_K^{-1}\chi_{g_0}\right)\right)}{\left(1 + p_D^{(c)}\xi_2 d'_{N_0}\right)\left(c'_K - Q_{1\,0}^{-1}C'_0\chi_K\right) + Q_{1\,0}^{-1}D'_0\chi_K}. \end{gathered} \tag{85}$$

For high pressures one obtains

$$\begin{gathered} R^0_{VIII\,C\infty} = R^0_{IV\,C\infty}, \qquad \Delta_{VIII\,C\infty} = \Delta_{IV\,C\infty}, \\ R^0_{VIII\,D\infty} = R^0_{IV\,D\infty}, \qquad \Delta_{VIII\,D\infty} = 1. \end{gathered} \tag{86}$$

Finally, let us consider case IX, where only unimolecular reaction paths are available ($P_C^{(c)} = P_D^{(c)} = 0$). For low pressure, reaction D is blocked and one obtains

$$R^0_{IX\,C0} = R_{I\,C0}, \quad \Delta_{IX\,C0} = \Delta_{I\,C0}. \tag{87}$$

For high pressure the corresponding results are

$$\begin{gathered} R^0_{IX\,C\infty} = -n_1\frac{P_C^{(u)}\chi_K}{Q_1} = -P_C^{(u)}X_K^{(qe)}, \qquad \Delta_{IX\,C\infty} = 1, \\ R^0_{IX\,D\infty} = -n_1\frac{P_D^{(u)}\chi_{g_m}}{Q_1} = -P_D^{(u)}X_{g_m}^{(qe)}, \qquad \Delta_{IX\,D\infty} = 1. \end{gathered} \tag{88}$$

This analysis shows that only for high pressure and purely unimolecular reactions, the non-equilibrium vibrational distribution does not affect the relationship between partial and total rate constants, i.e. the reaction rates are equilibrium. Only for this case the mass action law is valid. For all other cases a nonlinear dependence of the total rate constant on the partial reaction probabilities P_I, $I = C, D$ means violation of the mass action law.

Another important conclusion is the effect that arises from the collisional reactions: If $P_C^{(c)} = 0$, then $\Delta_{D\infty} = 1$ and $R^0_{C\infty}$ is equilibrium. In this case the non-equilibrium effects are caused only by the correlations and are all contained in the corresponding Δ-factors. These factors are determined by the collisional probability $P_D^{(c)}$. And vice versa, if $P_D^{(c)} = 0$, then $\Delta_{C\infty} = 1$ and $R^0_{D\infty}$ is equal to unity.

Possibility of blocking one of the parallel reactions is an important feature of the non-equilibrium system. From expression (67) for Δ_D it follows that the channel D is blocked when $g_0 \leq g_m$. This is the case in a low pressure limit and when $[M] < [M]_c$ and $P_C^{(u)} \neq 0$. For $P_C^{(u)} = 0$ one has $[M]_c = 0$ and reaction D is blocked only if collisional part of reaction C is rather intensive, i.e. $p_C^{(c)}\xi_C c'_K \geq \varepsilon_c^{(c)}$. Experimental study of this effect is of great interest.

5 Conclusions.

A general method of derivation of the gas-dynamic equations for non-equilibrium gas mixtures with internal degrees of freedom [1] was applied to study the effect of non-equilibrium on reaction rates. Its appropriateness was approved by comparison with the commonly accepted results on thermal dissociation of a small admixture. Unlike the previous approaches that could describe only weekly non-equilibrium situations (due to assumption of smallness of the part of the collisional integral responsible for the chemical reactions, see [12]) or spatially homogeneous situations for strongly non-equilibrium situations [6], our method is a consistent extension of the Chapman-Enskog method for gases with internal degrees of freedom. For the thermal dissociation process the influence of chemical reactions on the gas temperature has been discovered, that is described by the S-factor and appears in the expression for corresponding reaction rates. The same is for the exchange processes. For the parallel reactions this effect cannot be reduced to S-factor. Vibrational distributions appears to be the linear functions of all reaction rates, and more complex analysis is needed if these thermal effects are not negligible. This will be done elsewhere.

It is shown that accounting for both unimolecular and collisional channels of reactions significantly changes dependence of the reaction rates on pressure. Presence of the collisional reaction mechanism leads to a non-equilibrium behavior of reaction rates even at high pressures.

Under vibrational non-equilibrium conditions reaction rates are complicated functions of the reacting partners characteristics, even in the case of dissociating admixture in the mixture of inertial gases. Vibrational non-equilibrium causes strong correlations between reactions passing in parallel. One reaction can inhibit another, up to a complete blocking. Such correlations mean violation of the mass action law for the non-equilibrium mixtures. This necessitates reformulation of the chemical kinetic equations and new methods for their solution. This also makes challenging the procedure of the extraction reaction rates from experimental results.

Results obtained for the reaction rates confirm our predictions that the non-equilibrium affects mostly kinetic terms of the gas-dynamic equations, and not convective terms [1]. Significant influence of non-equilibrium on reaction rates is observed in the zero-order approximation, while such an influence on the transport properties (transport coefficient modification) will occur only in the higher-order approximation.

We plan to devote our further investigations to deriving of the two-temperature gas-dynamic equations for non-equilibrium gas mixtures, accounting for the temperature that characterizes internal molecule energy.

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Appendix A Kinetic equations for chemically reactive gases.

For the distribution function $F_\alpha(\mathbf{v}_\alpha, k_\alpha, \mathbf{r}, t)$ normalized to the number density the kinetic equation for chemically reactive gas mixture can be written in the form [11,13]

$$\frac{\partial F_\alpha}{\partial t} + \mathbf{v}_\alpha \cdot \nabla F_\alpha = I_\alpha,$$

$$I_\alpha = \sum_{\nu,\nu'}^{|\nu|\le 2 \vee |\nu'| \le 1} \sum_{k_\nu} \sum_{k_{\nu'}} \int' d\mathbf{v}_\nu \int' d\mathbf{v}_{\nu'} W^{\nu}_{\alpha,\nu'}\left(\mathbf{v}_\alpha, k_\alpha, \mathbf{v}_{\nu'}, k_{\nu'} | \mathbf{v}_\nu, k_\nu\right) \tag{A.1}$$

$$\times \left[\prod_{\beta\in\nu} \frac{F_\beta}{s_\beta(k_\beta)} - \frac{F_\alpha}{s_\alpha(k_\alpha)} \prod_{\beta\in\nu'} \frac{F_\beta}{s_\beta(k_\beta)} \right].$$

Here W is the transition probability; ν characterizes the reaction channel: $\nu = \{\nu_1, ..., \nu_\alpha, ...\}$, where ν_α is a number of particles of sort α in channel ν; $|\nu| = \nu_1 + ... + \nu_\alpha + ...$ is a number of particles in the channel ν; the summation is done over all pairs of channels for which the number of particles in the initial or final channel does not exceed two; $s_\alpha(k_\alpha)$ is a statistical weight of state k_α. Primes over integrals mean that the corresponding integration is done over different quantum states, aiming to avoid multiple account of the same states. For instance, if particles i and j are identical, the integral over velocities should be taken over the part of the velocity space as follows:

$$\int' d\mathbf{v}_\alpha d\mathbf{v}_{\alpha'} = \int\limits_{\mathbf{v}_\alpha < \mathbf{v}_{\alpha'}} d\mathbf{v}_\alpha d\mathbf{v}_{\alpha'},$$

where inequality should be realized componentwise. Transition probabilities satisfy the following microscopic reversibility law $W_{\nu}^{\nu'}(\mathbf{v}_\nu, k_\nu | \mathbf{v}_{\nu'}, k_{\nu'}) = W_{\nu'}^{\nu}(\mathbf{v}_{\nu'}, k_{\nu'} | \mathbf{v}_\nu, k_\nu)$.

While deriving kinetic equations for the systems with coupled states, the question concerning the definition of those states (molecules) arises. If only stable states are considered as coupled states (molecules), then the dissociation is possible only via the dual collisions, while recombination is possible only via triple collisions. In chemical physics, both in kinetics and in thermodynamics, it is generally accepted that particles in metastable states (resonances) with the time-of-life comparable with the mean free path are considered as molecules. Then it is necessary to consider the dissociation and recombination processes that occur via the intermediate metastable coupled states. These effects are taken into account in the aforecited kinetic equations. They are responsible for unimolecular reactions.

This kinetic equation satisfies the H-theorem. To prove it let us introduce the following expression for the entropy production σ of the quantity M which corresponds to the microscopic function ψ_α ($M = \langle \psi, F \rangle$)

$$\sigma_M = \langle \psi, I \rangle$$

$$= \sum_\alpha \sum_{\nu,\nu'}^{|\nu|\le 2 \vee |\nu'|\le 1} \sum_{k_\alpha, k_\nu, k_{\nu'}} \int d\mathbf{v}_\alpha \int' d\mathbf{v}_\nu \int' d\mathbf{v}_{\nu'} \psi_\alpha U^\nu_{\alpha,\nu'} \left(\mathbf{v}_\alpha, k_\alpha, \mathbf{v}_{\nu'}, k_{\nu'} | \mathbf{v}_\nu, k_\nu\right),$$

$$U^\nu_{\alpha,\nu'} = \textstyle\int' d\mathbf{v}_{\nu'} W^\nu_{\alpha,\nu'} \left(\mathbf{v}_\alpha, k_\alpha, \mathbf{v}_{\nu'}, k_{\nu'} | \mathbf{v}_\nu, k_\nu\right) \left[\prod_{\beta\in\nu} \frac{F_\beta}{s_\beta(k_\beta)} - \frac{F_\alpha}{s_\alpha(k_\alpha)} \prod_{\beta\in\nu'} \frac{F_\beta}{s_\beta(k_\beta)}\right],$$

Let us mention that

$$\textstyle\int d\mathbf{v}_\alpha \int' d\mathbf{v}_\nu \psi_\alpha U^\nu_{\alpha,\nu'} = \frac{1}{\nu!} \int d\mathbf{v}_\alpha \int d\mathbf{v}_\nu \psi_\alpha U^\nu_{\alpha,\nu'}$$

$$= \frac{1}{\nu_\alpha! \prod\limits_{\beta\neq\alpha} \nu_\beta!} \textstyle\int d\mathbf{v}_\alpha \int d\mathbf{v}_\nu \psi_\alpha U^\nu_{\alpha,\nu'} = \frac{1}{\nu_\alpha! \prod\limits_{\beta\neq\alpha} \nu_\beta!} \int d\mathbf{v}_\alpha \int d\mathbf{v}_\nu \psi_\alpha U^\nu_{\alpha,\nu'}$$

$$= \frac{\nu_\alpha + 1}{(\nu_\alpha + 1)! \prod\limits_{\beta\neq\alpha} \nu_\beta!} \textstyle\int d\mathbf{v}_\alpha \int d\mathbf{v}_\nu \psi_\alpha U^\nu_{\alpha,\nu'} = \nu''_\alpha \int' d\mathbf{v}_{\nu''} \psi_\alpha U^\nu_{\nu''},$$

where $\nu'' = \{1_\alpha, \nu'\}$. Using the symmetry of the $U^\nu_{\nu''}$ over identical particle interchanging, the last integral can be rewritten as

$$\nu''_\alpha \int' d\mathbf{v}_{\nu''} \psi_\alpha U^\nu_{\nu''} = \int' d\mathbf{v}_{\nu''} \sum_{i\in\nu''} \psi_\alpha(i) U^\nu_{\nu''},$$

where summation over i means the summation over all particles of sort α of the channel ν''. Hence

$$\sigma_M = \sum_{\nu,\nu''}^{|\nu|\vee|\nu''|\le 2} \sum_{k_\nu} \sum_{k_{\nu''}} \int' d\mathbf{v}_\nu \int' d\mathbf{v}_{\nu''} \psi_{\nu''} W^\nu_{\nu''} \left(\mathbf{v}_{\nu''}, k_{\nu''} | \mathbf{v}_\nu, k_\nu\right)$$

$$\times \left[\prod_{\beta\in\nu} \frac{F_\beta}{s_\beta} - \prod_{\beta\in\nu''} \frac{F_\beta}{s_\beta}\right], \qquad \psi_{\nu''} = \sum_{\beta\in\nu''} \psi_\beta.$$

Then the H-theorem is proved in a traditional way. The entropy in this case is defined as

$$S = -k \sum_{\alpha} \sum_{k_\alpha} \int d\mathbf{v}_\alpha F_\alpha \left(\mathbf{v}_\alpha, k_\alpha\right) \ln \frac{F_\alpha \left(\mathbf{v}_\alpha, k_\alpha\right)}{s_\alpha \left(k_\alpha\right) e}.$$

A mixture of dissociating molecules, of noble gases of two sorts and of the dissociation products is described by the following set of kinetic equations. Equation for the dissociating species has the form

$$\frac{\partial F_1}{\partial t} + \mathbf{v}_1 \cdot \nabla F_1 = I_1 = I_1^u + I_1^c + I_1^{nr}$$

$$= \sum_{k_4, k_5} \int' d\mathbf{v}_4 d\mathbf{v}_5 W_1^{4,5}(\mathbf{v}_1, k_1 | \mathbf{v}_4, k_4, \mathbf{v}_5, k_5) \left[\frac{F_4 \left(\mathbf{v}_4, k_4\right)}{s_4 \left(k_4\right)} \frac{F_5 \left(\mathbf{v}_5, k_5\right)}{s_5 \left(k_5\right)} - \frac{F_1 \left(\mathbf{v}_1, k_1\right)}{s_1 \left(k_1\right)} \right]$$

$$+ \sum_{\alpha=1}^{5} \sum_{k'_\alpha, k'_4, k'_5, k''_\alpha} \int' d\mathbf{v}'_\alpha d\mathbf{v}'_4 d\mathbf{v}'_5 d\mathbf{v}''_\alpha W_{1,\alpha}^{4,5,\alpha} \left(\mathbf{v}_1, k_1, \mathbf{v}'_\alpha, k'_\alpha | \mathbf{v}'_4, k'_4, \mathbf{v}'_5, k'_5, \mathbf{v}''_\alpha, k''_\alpha\right)$$

$$\times \left[\frac{F_4 \left(\mathbf{v}'_4, k'_4\right)}{s_4 \left(k'_4\right)} \frac{F_5 \left(\mathbf{v}'_5, k'_5\right)}{s_5 \left(k'_5\right)} \frac{F_\alpha \left(\mathbf{v}''_\alpha, k''_\alpha\right)}{s_\alpha \left(k''_\alpha\right)} - \frac{F_1(\mathbf{v}_1, k_1)}{s_1(k_1)} \frac{F_\alpha(\mathbf{v}'_\alpha, k'_\alpha)}{s_\alpha(k'_\alpha)} \right]$$

$$+ \sum_{k'_1, k''_1, k_4, k_5} \int' d\mathbf{v}'_1 d\mathbf{v}''_1 d\mathbf{v}_4 d\mathbf{v}_5 W_{1,4,5}^{1,1}(\mathbf{v}_1, k_1, \mathbf{v}_4, k_4, \mathbf{v}_5, k_5 | \mathbf{v}'_1, k'_1, \mathbf{v}''_1, k''_1)$$

$$\times \left[\frac{F_1 \left(\mathbf{v}'_1, k'_1\right)}{s_1 \left(k'_1\right)} \frac{F_1 \left(\mathbf{v}''_1, k''_1\right)}{s_1 \left(k''_1\right)} - \frac{F_1 \left(\mathbf{v}_1, k_1\right)}{s_1 \left(k_1\right)} \frac{F_4 \left(\mathbf{v}_4, k_4\right)}{s_4 \left(k_4\right)} \frac{F_5 \left(\mathbf{v}_5, k_5\right)}{s_5 \left(k_5\right)} \right]$$

$$+ \sum_{\alpha=1}^{5} \sum_{k'_1 k''_\alpha, k'_\alpha} \int' d\mathbf{v}' d\mathbf{v}''_\alpha d\mathbf{v}'_\alpha W_{1,\alpha}^{1,\alpha} \left(\mathbf{v}_1, k_1, \mathbf{v}'_\alpha, k'_\alpha | \mathbf{v}'_1, k'_1, \mathbf{v}''_\alpha, k''_\alpha\right)$$

$$\times \left[\frac{F_1 \left(\mathbf{v}'_1, k'_1\right)}{s_1 \left(k'_1\right)} \frac{F_\alpha \left(\mathbf{v}''_\alpha, k''_\alpha\right)}{s_\alpha \left(k''_\alpha\right)} - \frac{F_1 \left(\mathbf{v}_1, k_1\right)}{s_1 \left(k_1\right)} \frac{F_\alpha \left(\mathbf{v}'_\alpha, k'_\alpha\right)}{s_\alpha \left(k'_\alpha\right)} \right].$$

Here subindex 1 denotes the dissociating species, subindexes 2 and 3 denote the noble gas species, while subindexes 4 and 5 denote the dissociation reaction products. Term I_1^u describes the metastable molecules decay via unimolecular reactions and their formation due to dissociation products agglomeration. Term I_1^c describes the dissociation and recombination reactions occurring in three-particle collisions. It consists of two items. The first one corresponds to the situation when particles of sort 1 are formed in the state $\{\mathbf{v}_1, k_1\}$ during agglomeration (recombination) in three particle collisions and escape this state during dissociation. In these two reactions any particle, including 1, can be a collisional partner. The second item corresponds to the situation when the collisional partner only of sort 1 is considered. In recombination reaction it can leave the state $\{\mathbf{v}_1, k_1\}$ and therefore the corresponding term presents with sign "$-$". In dissociation the partner-particle can occupy the state $\{\mathbf{v}_1, k_1\}$ and therefore contribute to the incoming process. Term I_1^{nr} describes the nonreactive dual collisions.

Equations for noble gases have the form

$$\frac{\partial F_\alpha}{\partial t} + \mathbf{v}_\alpha \cdot \nabla F_\alpha = I_\alpha = I_\alpha^c + I_\alpha^{nr}$$

$$= \sum_{k'_\alpha, k'_4, k'_5} \int' d\mathbf{v}'_\alpha d\mathbf{v}'_4 d\mathbf{v}'_5 W_{\alpha,1}^{\alpha,4,5}(\mathbf{v}_\alpha, k_\alpha, \mathbf{v}_1, k_1 | \mathbf{v}'_\alpha, k'_\alpha, \mathbf{v}'_4, k'_4, \mathbf{v}'_5, k'_5)$$

$$\times \left[\frac{F_4(\mathbf{v}'_4, k'_4}{s_4(k'_4)} \frac{F_5(\mathbf{v}'_5, k'_5)}{s_5(k'_5)} \frac{F_\alpha(\mathbf{v}'_\alpha, k'_\alpha)}{s_\alpha(k'_\alpha)} - \frac{F_1(\mathbf{v}_1, k_1)}{s_1(k_1)} \frac{F_\alpha(\mathbf{v}_\alpha, k_\alpha)}{s_\alpha(k_\alpha)} \right]$$

$$+ \sum_{k'_\alpha, k'_4, k'_5} \int' d\mathbf{v}'_\alpha d\mathbf{v}'_4 d\mathbf{v}'_5 W_{\alpha,4,5}^{\alpha,1}(\mathbf{v}_\alpha, k_\alpha, \mathbf{v}_4, k_4, \mathbf{v}_5, k_5 | \mathbf{v}'_\alpha, k'_\alpha, \mathbf{v}'_1, k'_1)$$

$$\times \left[\frac{F_1(\mathbf{v}'_1, k'_1)}{s_1(k'_1)} \frac{F_\alpha(\mathbf{v}'_\alpha, k'_\alpha)}{s_\alpha(k'_\alpha)} - \frac{F_4(\mathbf{v}_4, k_4)}{s_4(k_4)} \frac{F_5(\mathbf{v}_5, k_5)}{s_5(k_5)} \frac{F_\alpha(\mathbf{v}_\alpha, k_\alpha)}{s_\alpha(k_\alpha)} \right]$$

$$+ \sum_{\beta=1}^{5} \sum_{k'_\beta, k''_\beta k'_\alpha} \int' d\mathbf{v}'_\beta d\mathbf{v}''_\beta d\mathbf{v}'_\alpha W_{\beta,\alpha}^{\beta,\alpha} \left(\mathbf{v}'_\beta, k'_\beta, \mathbf{v}_\alpha, k_\alpha | \mathbf{v}''_\beta, k''_\beta, \mathbf{v}'_\alpha, k'_\alpha \right)$$

$$\times \left[\frac{F_\beta(\mathbf{v}''_\beta, k''_\beta)}{s_\beta(k''_\beta)} \frac{F_\alpha(\mathbf{v}'_\alpha, k'_\alpha)}{s_\alpha(k'_\alpha)} - \frac{F_\beta(\mathbf{v}'_\beta, k'_\beta)}{s_\beta(k'_\beta)} \frac{F_\alpha(\mathbf{v}_\alpha, k_\alpha)}{s_\alpha(k_\alpha)} \right], \qquad \alpha = 2, 3.$$

Here the first term, I_α^c, describes the collisional dissociation and recombination. As previously, it consists of two parts. The first one describes the situation when particles of sort α, playing the role of collisional partners, are formed in the state $\{\mathbf{v}_\alpha, k_\alpha\}$ in recombination process and leave this state in the dissociation reaction. The second one describes the opposite situation. Term I_α^{nr} describes the nonreactive dual collisions.

Equations for the dissociation products can be written as

$$\frac{\partial F_\alpha}{\partial t} + \mathbf{v}_\alpha \cdot \nabla F_\alpha = I_\alpha = I_\alpha^u + I_\alpha^c + I_\alpha^{nr}$$

$$= \sum_{k_1,k_\beta} \int' d\mathbf{v}_1 d\mathbf{v}_\beta W^1_{\alpha,\beta}(\mathbf{v}_1, k_1 | \mathbf{v}_\alpha, k_\alpha, \mathbf{v}_\beta, k_\beta)$$

$$\times \left[\frac{F_1(\mathbf{v}_1, k_1)}{s_1(k_1)} - \frac{F_\alpha(\mathbf{v}_\alpha, k_\alpha)}{s_\alpha(k_\alpha)} \frac{F_\beta(\mathbf{v}_\beta, k_\beta)}{s_\beta(k_\beta)} \right]$$

$$+ \sum_{\gamma=1}^{5} \sum_{k_\beta, k''_\gamma, k'_\alpha, k_1} \int' d\mathbf{v}_\beta d\mathbf{v}''_\gamma d\mathbf{v}'_\alpha d\mathbf{v}_1 W^{\alpha,1}_{\alpha,\beta,\gamma}(\mathbf{v}_\alpha, k_\alpha, \mathbf{v}_\beta, k_\beta, \mathbf{v}''_\gamma, k''_\gamma | \mathbf{v}'_\alpha, k'_\alpha, \mathbf{v}_1, k_1)$$

$$\times \left[\frac{F_1(\mathbf{v}_1, k_1)}{s_1(k_1)} \frac{F_\alpha(\mathbf{v}'_\alpha, k'_\alpha)}{s_\alpha(k'_\alpha)} - \frac{F_\alpha(\mathbf{v}_\alpha, k_\alpha)}{s_\alpha(k_\alpha)} \frac{F_\beta(\mathbf{v}_\beta, k_\beta)}{s_\beta(k_\beta)} \frac{F_\gamma(\mathbf{v}''_\gamma, k''_\gamma)}{s_\gamma(k''_\gamma)} \right]$$

$$+ \sum_{k_1, k'_\alpha, k_\beta, k''_\gamma} \int' d\mathbf{v}_1 d\mathbf{v}'_\alpha d\mathbf{v}_\beta d\mathbf{v}''_\gamma W^{\alpha,\beta,\gamma}_{\alpha,1}(\mathbf{v}_\alpha, k_\alpha, \mathbf{v}_1, k_1 | \mathbf{v}'_\alpha, k'_\alpha, \mathbf{v}_\beta, k_\beta, \mathbf{v}''_\gamma, k''_\gamma)$$

$$\times \left[\frac{F_\alpha(\mathbf{v}'_\alpha, k'_\alpha)}{s_\alpha(k'_\alpha)} \frac{F_\gamma(\mathbf{v}''_\gamma, k''_\gamma)}{s_\gamma(k''_\gamma)} \frac{F_\beta(\mathbf{v}_\beta, k_\beta)}{s_\beta(k_\beta)} - \frac{F_1(\mathbf{v}_1, k_1)}{s_1(k_1)} \frac{F_\alpha(\mathbf{v}_\alpha, k_\alpha)}{s_\alpha(k_\alpha)} \right]$$

$$+ \sum_{\gamma=1}^{5} \sum_{k'_\gamma, k''_\gamma k'_\alpha} \int' d\mathbf{v}'_\gamma d\mathbf{v}''_\gamma d\mathbf{v}'_\alpha W^{\gamma,\alpha}_{\gamma,\alpha} \left(\mathbf{v}'_\gamma, k'_\gamma, \mathbf{v}_\alpha, k_\alpha | \mathbf{v}''_\gamma, k''_\gamma, \mathbf{v}'_\alpha, k'_\alpha \right)$$

$$\times \left[\frac{F_\gamma(\mathbf{v}''_\gamma, k''_\gamma)}{s_\gamma(k''_\gamma)} \frac{F_\alpha(\mathbf{v}'_\alpha, k'_\alpha)}{s_\alpha(k'_\alpha)} - \frac{F_\gamma(\mathbf{v}'_\gamma, k'_\gamma)}{s_\gamma(k'_\gamma)} \frac{F_\alpha(\mathbf{v}_\alpha, k_\alpha)}{s_\alpha(k_\alpha)} \right],$$

$$\alpha = 4, 5, \quad \beta = 4, 5, \quad \alpha \neq \beta.$$

Term I^u_α describes unimolecular decay and molecular formation due to dissociation products agglomeration. Term I^c_α describes the dissociation and recombination reactions occurring in the three-particle collisions. It consists of two items (similar to those described above). Term I^{nr}_α describes the nonreactive collisions.

Appendix B Equations for vibrational population densities.

To solve Eq. (7) we simplify it by assuming that due to short relaxation time both translational and rotational distributions remain Maxwell-Boltzmann ones (13).

Then after substituting $F_\alpha^{(e)TR} X_\alpha(n_\alpha)$ into collisional integral one obtains

$$I_\alpha\left(F\right) = \sum_{\nu,\nu'}^{|\nu|\vee(|\nu'|+1_\alpha)\leq 2} \sum_{k_\nu} \sum_{k_{\nu'}} \int' d\mathbf{v}_\nu \int' d\mathbf{v}_{\nu'} W^\nu_{\alpha,\nu'}\left(\mathbf{v}_\alpha, k_\alpha, \mathbf{v}_{\nu'}, k_{\nu'} | \mathbf{v}_\nu, k_\nu\right)$$

$$\times \left[\prod_{\beta\in\nu} \frac{F_\beta^{(e)TR} X_\beta}{s_\beta} - \frac{F_\alpha^{(e)TR} X_\alpha}{s_\alpha} \prod_{\beta\in\nu'} \frac{F_\beta^{(e)TR} X_\beta}{s_\beta} \right].$$

Integration over $\mathbf{v}_\alpha$ and summation over j_α gives

$$\tilde{I}_\alpha(X_\alpha) \equiv \sum_{j_\alpha} \int d\mathbf{v}_\alpha I_\alpha\left(F\right)$$

$$= \sum_{\nu,\nu'}^{|\nu|\leq 2\vee|\nu'|\leq 1} \sum_{k_\nu} \sum_{k_{\nu'}} \sum_{j_\alpha} \int d\mathbf{v}_\alpha \int' d\mathbf{v}_\nu \int' d\mathbf{v}_{\nu'} W^\nu_{\alpha,\nu'}\left(\mathbf{v}_\alpha, k_\alpha, \mathbf{v}_{\nu'}, k_{\nu'} | \mathbf{v}_\nu, m_\nu\right)$$

$$\times \left[\prod_{\beta\in\nu} \frac{F_\beta^{(e)TR} X_\beta}{s_\beta} - \frac{F_\alpha^{(e)TR} X_\alpha}{s_\alpha} \prod_{\beta\in\nu'} \frac{F_\beta^{(e)TR} X_\beta}{s_\beta} \right]$$

The first term of the collisional integral can be rewritten as

$$\sum_{\nu,\nu'}^{|\nu|\leq 2\vee|\nu'|\leq 1} \sum_{j_\nu, n_\nu} \sum_{j_{\nu'}, n_{\nu'}} \sum_{j_\alpha} \int d\mathbf{v}_\alpha \int' d\mathbf{v}_\nu \int' d\mathbf{v}_{\nu'} W^\nu_{\alpha,\nu'}\left(\mathbf{v}_\alpha, j_\alpha, n_\alpha, \mathbf{v}_{\nu'}, j_{\nu'}, n_{\nu'} | \mathbf{v}_\nu, j_\nu, n_\nu\right)$$

$$\times \exp\left[-\frac{e_\nu^{(T)} + e_\nu^{(R)} + e_\nu^{(RV)}}{kT} \right] \prod_{\beta\in\nu} \frac{1}{Q_\beta^{(RT)}(n_\beta) s_\beta^{(V)}(n_\beta)} X_\beta(n_\beta)$$

$$= \sum_{\nu,\nu'}^{|\nu|\leq 2\vee|\nu'|\leq 1} \sum_{n_\nu} \sum_{n_{\nu'}} \eta_\alpha(\alpha,\nu') W^\nu_{\alpha,\nu'}\left(n_\alpha, n_{\nu'} | n_\nu\right) \prod_{\beta\in\nu} \frac{X_\beta(n_\beta)}{s_\beta^{(V)}(n_\beta)}, \qquad e_\nu = \sum_{\beta\in\nu} e_\beta.$$

Here $\eta_\alpha(\alpha,\nu')$ is a number of particles of sort α in channel $\{\alpha,\nu'\}$, and averaged vibrational transition probabilities are defined as

$$W^\nu_{\alpha,\nu'}\left(n_\alpha, n_{\nu'} | n_\nu\right) = \sum_{j_\nu, j_{\nu'}, j_\alpha} \int' d\mathbf{v}_\alpha d\mathbf{v}_\nu \int' d\mathbf{v}_{\nu'}$$

$$\times W^\nu_{\alpha,\nu'}\left(\mathbf{v}_\alpha, j_\alpha, n_\alpha, \mathbf{v}_{\nu'}, j_{\nu'}, n_{\nu'} | \mathbf{v}_\nu, j_\nu, n_\nu\right) \tag{B.1}$$

$$\times \exp\left[-\frac{e_\nu^{(T)} + e_\nu^{(R)} + e_\nu^{(RV)}}{kT} \right] \prod_{\beta\in\nu} \frac{1}{Q_\beta^{(TR)}\left(n_\beta\right)},$$

or in more symmetrical way

$$W_{\nu'}^{\nu}\left(n_{\nu'}|n_{\nu}\right)=\sum_{j_\nu}\sum_{j_{\nu'}}\int' d\mathbf{v}_\nu\int' d\mathbf{v}_{\nu'}W_{\nu'}^{\nu}\left(\mathbf{v}_{\nu'},j_{\nu'},n_{\nu'}|\mathbf{v}_\nu,j_\nu,n_\nu\right)$$

$$\times\exp\left[-\frac{e_\nu^{(T)}+e_\nu^{(R)}+e_\nu^{(RV)}}{kT}\right]\prod_{\beta\in\nu}\frac{1}{Q_\beta^{(TR)}(n_\beta)}.$$

The second term in the collisional integral has the form

$$\sum_{\nu,\nu'}^{|\nu|\le 2\vee|\nu|'\le 1}\ \sum_{j_\nu,n_\nu}\sum_{j_{\nu'},n_{\nu'}}\sum_{j_\alpha}\int d\mathbf{v}_\alpha\int' d\mathbf{v}_\nu\int' d\mathbf{v}_{\nu'}W_{\nu}^{\alpha,\nu'}\left(\mathbf{v}_\nu,j_\nu,n_\nu|\mathbf{v}_\alpha,j_\alpha,n_\alpha,\mathbf{v}_{\nu'},j_{\nu'},n_{\nu'}\right)$$

$$\times\exp\left[-\frac{e_{\alpha,\nu'}^{(T)}+e_{\alpha,\nu'}^{(R)}+e_{\alpha,\nu'}^{(RV)}}{kT}\right]\frac{X_\alpha}{Q_\alpha^{(TR)}\left(n_\alpha\right)s_\alpha^{(V)}\left(n_\alpha\right)}\prod_{\beta\in\nu'}\frac{X_\beta}{Q_\beta^{(TR)}\left(n_\beta\right)s_\beta^{(V)}\left(n_\beta\right)}$$

$$=\sum_{\nu,\nu'}^{|\nu|\le 2\vee|\nu|'\le 1}\ \sum_{n_\nu}\sum_{n_{\nu'}}\eta_\alpha(\alpha,\nu')W_{\nu}^{\alpha,\nu'}\left(n_\nu|n_\alpha,n_{\nu'}\right)\frac{X_\alpha}{s_\alpha^{(V)}\left(n_\alpha\right)}\prod_{\beta\in\nu'}\frac{X_\beta}{s_\beta^{(V)}\left(n_\beta\right)}.$$

Here the microscopic reversibility principle

$$W_{\nu'}^{\nu}\left(\mathbf{v}_{\nu'},j_{\nu'},n_{\nu'}|\mathbf{v}_\nu,j_\nu,n_\nu\right)=W_{\nu}^{\nu'}\left(\mathbf{v}_\nu,j_\nu,n_\nu|\mathbf{v}_{\nu'},j_{\nu'},n_{\nu'}\right),\tag{B.2}$$

was used.

Thus the collisional operator applied to the vibration populations has the form

$$\tilde{I}_\alpha\left(X\right)=\sum_{\nu,\nu'}^{|\nu|\le 2\vee|\nu|'\le 1}\ \sum_{n_\nu}\sum_{m_{\nu'}}\eta_\alpha(\alpha,\nu')$$

$$\times\left[W_{\alpha,\nu'}^{\nu}\left(n_\alpha,n_{\nu'}|n_\nu\right)\prod_{\beta\in\nu}\frac{X_\beta}{s_\beta^{(V)}\left(n_\beta\right)}-W_{\nu}^{\alpha,\nu'}\left(n_\nu|n_\alpha,n_{\nu'}\right)\frac{X_\alpha}{s_\alpha^{(V)}\left(n_\alpha\right)}\prod_{\beta\in\nu'}\frac{X_\beta}{s_\beta^{(V)}\left(n_\beta\right)}\right].$$

Using definition (B.1), the energy conservation law $e_\nu=e_{\nu'}$ (see (11), $e_\nu=\sum\limits_{\beta\in\nu}e_\beta$), and the equality (B.2), one can write

$$W_{\nu'}^{\nu}\left(n_{\nu'}|n_{\nu}\right)=\sum_{j_\nu}\sum_{j_{\nu'}}\int' d\mathbf{v}_\nu\int' d\mathbf{v}_{\nu'}W_{\nu'}^{\nu}\left(\mathbf{v}_{\nu'},j_{\nu'},n_{\nu'}|\mathbf{v}_\nu,j_\nu,n_\nu\right)$$

$$\times\exp\left[-\frac{e_\nu^{(T)}+e_\nu^{(R)}+e_\nu^{(RV)}}{kT}\right]\prod_{\beta\in\nu}\frac{1}{Q_\beta^{(RT)}\left(n_\beta\right)}$$

$$=\sum_{j_\nu}\sum_{j_{\nu'}}\int' d\mathbf{v}_\nu\int' d\mathbf{v}_{\nu'}W_{\nu}^{\nu'}\left(\mathbf{v}_\nu,j_\nu,n_\nu|\mathbf{v}_{\nu'},j_{\nu'},n_{\nu'}\right)\times \tag{B.3}$$

$$\exp\left[-\frac{e_{\nu'}^{(T)}+e_{\nu'}^{(R)}+e_{\nu'}^{(RV)}+\left(e_{\nu'}^{(0)}+e_{\nu'}^{(V)}\right)-\left(e_{\nu}^{(0)}+e_{\nu}^{(V)}\right)}{kT}\right]\frac{1}{\prod\limits_{\beta\in\nu}Q_\beta^{(TR)}\left(n_\beta\right)}$$

$$=W_{\nu}^{\nu'}\left(n_\nu|n_{\nu'}\right)\exp\left[-\frac{\left(e_{\nu'}^{(0)}+e_{\nu'}^{(V)}\right)-\left(e_{\nu}^{(0)}+e_{\nu}^{(V)}\right)}{kT}\right]\frac{\prod\limits_{\beta\in\nu'}Q_\beta^{(TR)}\left(n_\beta\right)}{\prod\limits_{\beta\in\nu}Q_\beta^{(TR)}\left(n_\beta\right)}.$$

This equality is called a detailed balance relation. It has nontrivial dependence on the vibration levels due to the ratio of the statistical sums. This ratio holds true for the case without chemical reactions but for coupled rotations and vibrations. Without such coupling ($e_\alpha^{(RV)}=0$, $s_\alpha^{(RV)}=1$) relation (B.3) reduces to (18).

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