

On the First Order Chemical Reaction Rates in Non-Equilibrium Gas Flows

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Abstract. A mathematical model for reaction rates in non-equilibrium viscous gas flows is proposed on the basis of the kinetic theory methods. First order corrections to the dissociation rate coefficients taking into account non-Maxwell velocity distributions and gas flow non-homogeneity and compressibility are derived for the case of thermal equilibrium one-temperature flows. Relations of the reaction rate coefficients to the bulk viscosity coefficient and relaxation pressure are established for non-equilibrium viscous flows of binary mixtures. First order correction to the reaction rates is estimated for expanding N₂/N mixture flows.

Keywords: Kinetic theory, Chemical reaction rates, Transport coefficients, Non-equilibrium reactive flows

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INTRODUCTION

The paper deals with modeling of non-equilibrium reaction rates in gas flows. Originally, starting from Prigogine [1], the rates of chemical reactions were studied for space-homogeneous gases. Later, for the simulation of reacting gas flows, fluid dynamic equations have been coupled to the equations of chemical kinetics in a flow, and an important role of reaction rates in gas dynamics has been recognized. Global reaction rates in different thermally non-equilibrium gas flows were investigated on the basis of state-to-state vibrational distributions and state-dependent rate coefficients of elementary processes [2, 3, 4, 5], and it was shown that non-equilibrium reaction rate coefficients are far from the ones given by the Arrhenius law.

It should be noted, that up to the present day, mainly the zero order reaction rate coefficients corresponding to the Maxwell distribution over velocities are used in aerodynamic applications: indeed, the zero order coefficients are inserted to the CFD codes for the calculation of gas flow parameters in both inviscid Euler and viscous Navier-Stokes approximations. Rigorously speaking, for the correct realization of the Navier-Stokes approximation, the non-maxwellian first order reaction rate coefficients are required [6]. Different approaches of the kinetic theory, based on the generalization of the Chapman-Enskog method [7, 8, 9, 10, 11, 12, 13] or linear thermodynamics [14] were developed for modeling of the reaction rates. General algorithms for the calculation of the reaction rate coefficients in the state-to-state, multi-temperature and one-temperature approaches were proposed in [6, 10]. In these Refs, contributions to the reaction rates due to space non-homogeneity and non-maxwellian velocity distributions are shown. Moreover, in [14], on the basis of the linear thermodynamic method, the expressions for the one-temperature reaction rates are proposed in the form showing explicitly the contribution of gas compressibility. However, no numerical estimations of the first order terms in the expressions for the reaction rate coefficients have been performed, and contrasting opinions about the importance of coupling the first order rates and fluid dynamic equations persist up to now.

The aim of the present paper is to clarify this problem and study the first order corrections to the one-temperature reaction rate coefficients in a moving gas mixture on the basis of the kinetic theory methods developed in [6]. Strong non-equilibrium chemical kinetics in a flow is considered under the conditions of local thermal equilibrium. In this case, the characteristic times of various elementary processes satisfy to the relation

$$\tau_{lr} < \tau_{int} \ll \tau_{react} \sim \theta. \quad (1)$$

Here τ_{lr} , τ_{int} , τ_{react} are the characteristic times of elastic collisions, relaxation of internal energy and chemical reactions; θ is the mean time of gas dynamic parameters change.

Based on relation (1), a closed self-consistent flow description is developed using the formalism of the Chapman-Enskog method modified for gas mixtures with rapid and slow processes [6]. General expressions for the first order transport terms and reaction rates are derived; for a binary mixture, relations between transport coefficients and first order rate coefficients are established. Dimensionless parameters determining the order of magnitude of the first order corrections are introduced and then estimated for a non-equilibrium expanding N_2/N mixture flow.

THEORETICAL MODEL

Under condition (1), a closed flow description is given by the following set of macroscopic equations:

$$\rho \frac{d\alpha_c}{dt} + \nabla \cdot \mathbf{J}_{m_c} = \sum_r \dot{\xi}_r \nu_{rc} M_c, \quad c = 1, \dots, L, \quad (2)$$

$$\rho \frac{d\mathbf{v}}{dt} + \nabla \cdot \mathbf{P} = 0, \quad (3)$$

$$\rho \frac{du}{dt} + \nabla \cdot \mathbf{J}_U + \mathbf{P} : \nabla \mathbf{v} = 0. \quad (4)$$

Here ρ is the density, α_c is the component c mass fraction, \mathbf{v} is the gas velocity, u is the internal energy per unit total mass, \mathbf{J}_{m_c} is the component mass diffusive flux, \mathbf{J}_U is the internal energy diffusive flux, \mathbf{P} is the pressure tensor, M_c is the component molar mass, $\dot{\xi}_r$ is the chemical reaction rate, ν_{rc} are the global stoichiometric coefficients, L is the number of components. Introducing the rate coefficients of forward and backward reactions $k_{f,r}$, $k_{b,r}$, the reaction rate $\dot{\xi}_r$ can be written in the conventional form:

$$\dot{\xi}_r = k_{f,r} \prod_{c=1}^L \left(\frac{\rho_c}{M_c} \right)^{\nu_{rc}^{(r)}} - k_{b,r} \prod_{c=1}^L \left(\frac{\rho_c}{M_c} \right)^{\nu_{rc}^{(p)}}, \quad (5)$$

$\nu_{rc}^{(r)}$, $\nu_{rc}^{(p)}$ are the stoichiometric coefficients of reactants and products.

Transport and production terms in Eqs. (2)–(4) are defined in terms of the distribution functions f_{cij} of a component c at the vibrational and rotational levels i , j . Thus, for the dissociation reaction, expression for $k_{f,r}$ reads

$$\nu_{diss,c} k_{f,diss} = N_A \sum_{jl} \sum_{ik} \int \frac{f_{cij} f_{dkl}}{n_c n_d} g \sigma_{cij,d}^{diss} d\mathbf{u}_c d\mathbf{u}_d d\mathbf{u}_{c'} d\mathbf{u}_{f'} d\mathbf{u}'_d, \quad (6)$$

$\nu_{diss,c}$ is the global stoichiometric coefficient of dissociation reaction, N_A is the Avogadro number, n_c is the number density of component c , g is the relative velocity of particles, $\sigma_{cij,d}^{diss}$ is the formal cross section of the collisions with dissociation, \mathbf{u}_c , \mathbf{u}_d are the reagents velocities, $\mathbf{u}_{c'}$, $\mathbf{u}_{f'}$, \mathbf{u}'_d are the products velocities.

In the zero order approximation of the Chapman-Enskog method, distribution functions take the form of Maxwell-Boltzmann distributions over velocity and internal energy. The transport terms reduce to

$$\mathbf{J}_{m_c} = 0, \quad \mathbf{J}_U = 0, \quad \mathbf{P} = p\mathbf{I}, \quad (7)$$

\mathbf{I} is the unit tensor. If the cross sections of reactive collisions are known, the zero order reaction rate coefficients can be easily calculated substituting the Maxwell-Boltzmann distributions to expressions (6):

$$\nu_{diss,c} k_{f,diss}^{(0)}(T) = \frac{4\pi N_A}{Z_c^{int}(T)} \left(\frac{m_{cd}}{2\pi kT} \right)^{3/2} \sum_{ij} \int \exp \left(-\frac{m_{cd} g^2}{2kT} \right) s_{ij}^c \exp \left(-\frac{\epsilon_{ij}^c}{kT} \right) g^3 \sigma_{cij,d}^{diss}(g, \mathbf{u}_{c'}, \mathbf{u}_{f'}, \mathbf{u}'_d) dg d\mathbf{u}_{c'} d\mathbf{u}_{f'} d\mathbf{u}'_d, \quad (8)$$

m_{cd} is the reduced mass of colliding particles, k is the Boltzmann constant, T is the temperature, ϵ_{ij}^c , s_{ij}^c are the internal energy and statistical weight of the state i and j , Z_c^{int} is the internal partition function. For practical applications, instead of expression (8), the empirical Arrhenius law is commonly used with parameters retrieved from experiments; forward and backward reaction rates are connected through the equilibrium constant. One should however keep in mind that using of the Arrhenius law is limited by the particular kinds of molecules.

FIRST ORDER SOLUTION

The first order correction to the distribution function in the one-temperature approach is found in the form [6]

$$f_{cij}^{(1)} = f_{cij}^{(0)} \left(-\frac{1}{n} \mathbf{A}_{cij} \cdot \nabla \ln T - \frac{1}{n} \sum_d \mathbf{D}_{cij}^d \cdot \mathbf{d}_d - \frac{1}{n} \mathbf{B}_{cij} : \nabla \mathbf{v} - \frac{1}{n} F_{cij} \nabla \cdot \mathbf{v} - \frac{1}{n} G_{cij} \right). \quad (9)$$

Here \mathbf{d}_c is the diffusive driving force, functions \mathbf{A}_{cij} , \mathbf{B}_{cij} , \mathbf{D}_{cij}^d , F_{cij} and G_{cij} satisfy the linear integral equations given in [6].

Let us consider the expressions for transport and source terms in Eqs. (2)–(4) corresponding to the first order distribution functions (9). Pressure tensor has a form:

$$\mathbf{P} = (p - p_{rel}) \mathbf{I} - 2\eta \mathbf{S} - \zeta \nabla \cdot \mathbf{v} \mathbf{I}, \quad (10)$$

\mathbf{S} is the deformation rate tensor, p_{rel} , η and ζ are the relaxation pressure, bulk and shear viscosity coefficients:

$$\eta = \frac{kT}{10} [\mathbf{B}, \mathbf{B}], \quad \zeta = kT [F, F], \quad p_{rel} = kT [F, G]. \quad (11)$$

Bracket integrals in (11) contain the cross sections of collisions in rapid processes (elastic collisions and inelastic ones with internal energy transitions) and are introduced in a traditional way [6].

Mass and internal energy diffusive fluxes are found as follows:

$$\mathbf{J}_{m_c} = \rho_c \mathbf{w}_c, \quad \mathbf{w}_c = - \sum_d D_{cd} \mathbf{d}_d - D_{Tc} \nabla \ln T, \quad (12)$$

$$\mathbf{J}_U = -\lambda' \nabla T - p \sum_c D_{Tc} \mathbf{d}_c + \sum_c h_c \mathbf{J}_{m_c}, \quad (13)$$

diffusion, thermal diffusion and heat conductivity coefficients are given by

$$D_{cd} = \frac{1}{3n} [\mathbf{D}^c, \mathbf{D}^d], \quad D_{Tc} = \frac{1}{3n} [\mathbf{D}^c, \mathbf{A}], \quad \lambda' = \frac{k}{3} [\mathbf{A}, \mathbf{A}]. \quad (14)$$

Chemical reaction rates in Eqs. (2) in the first order approximation have the form (5), where rate coefficients are obtained substituting the first order distribution function (9) to the definition (6). Thus dissociation rate coefficient reads

$$k_{f,diss} = k_{f,diss}^{(0)}(T) - k_{f,diss}^{(1)}(\alpha_1, \dots, \alpha_L, T) - k_{f,diss}^{(2)}(\alpha_1, \dots, \alpha_L, T). \quad (15)$$

First order corrections to the rate coefficients are given by the expressions:

$$v_{diss,c} k_{f,diss}^{(1)} = N_A \sum_{ik\bar{i}k'} \sum_{jl\bar{j}l'} \int \frac{f_{cij}^{(0)} f_{dkl}^{(0)}}{n_c n_d} (G_{cij} + G_{dkl}) g \sigma_{cij,d}^{diss} d\mathbf{u}_c d\mathbf{u}_d d\mathbf{u}_{c'} d\mathbf{u}_{f'} d\mathbf{u}_d', \quad (16)$$

$$v_{diss,c} k_{f,diss}^{(2)} = \nabla \cdot \mathbf{v} N_A \sum_{ik\bar{i}k'} \sum_{jl\bar{j}l'} \int \frac{f_{cij}^{(0)} f_{dkl}^{(0)}}{n_c n_d} (F_{cij} + F_{dkl}) g \sigma_{cij,d}^{diss} d\mathbf{u}_c d\mathbf{u}_d d\mathbf{u}_{c'} d\mathbf{u}_{f'} d\mathbf{u}_d'. \quad (17)$$

Quantities $k_{f,diss}^{(1)}$, $k_{f,diss}^{(2)}$ express first order corrections to the thermal equilibrium rate coefficients (8). The first coefficients appear due to deviations from Maxwell-Boltzmann distributions over velocities and internal energies whereas the last ones containing $\nabla \cdot \mathbf{v}$ are due to spatial non-homogeneity. If internal degrees of freedom are neglected, coefficients $k_{f,diss}^{(2)}$ vanish.

Using the expansions of functions \mathbf{A}_{cij} , \mathbf{B}_{cij} , \mathbf{D}_{cij}^d , F_{cij} and G_{cij} into the finite series of Sonine and Waldmann-Trübenbacher orthogonal polynomials, one can obtain linear transport systems for definition of transport coefficients and p_{rel} [6]. Coefficients $k_{f,diss}^{(1)}$, $k_{f,diss}^{(2)}$ are associated to the scalar functions F_{cij} , G_{cij} and therefore, in principle, can be connected to the bulk viscosity coefficient and relaxation pressure determined by the same functions (see (11)). For the general case, derivation of such a relationship represents a difficult task. For a binary mixture, the relation between transport and rate coefficients is established in the next section.

BINARY MIXTURE N₂/N

In this section, a binary N₂/N mixture is considered with two elementary reactions



For binary mixtures, transport linear systems derived in [6] for the calculation of scalar functions F_{cij} , G_{cij} can be simplified. This allows one to find relations connecting bulk viscosity coefficients and relaxation pressure to the first order dissociation rate coefficients. Let us introduce partial relaxation pressures $p_{rel,c}$ and fictive bulk viscosity coefficients of species ζ_c by expressions

$$p_{rel} = x_{N_2} p_{rel,N_2} + x_N p_{rel,N}, \quad \zeta = x_{N_2} \zeta_{N_2} + x_N \zeta_N, \quad (20)$$

$x_c = n_c/n$ is the molar fraction of species c .

Now, similarly to commonly used in the transport theory $\Omega_{cd}^{(r,p)}$ -integrals over cross sections of rapid processes, one can define generalized $\tilde{\Omega}$ -integrals depending on the cross sections of slow processes. In the present case, we introduce the integral operators associated to the dissociation cross sections:

$$\tilde{\Omega}_{cd}^{diss(r,p)} = \left(\frac{kT}{2\pi m_{cd}} \right)^{1/2} \sum_{ikl'k'} \sum_{jl'j'l'} \frac{s_{ij}^c s_{kl}^d}{Z_c^{int} Z_d^{int}} \int \gamma^{2r+3} (\mathcal{E}_{ij}^c)^p \exp(-\gamma^2 - \mathcal{E}_{ij}^c - \mathcal{E}_{kl}^d) \sigma_{cij,d}^{diss} d\mathbf{u}_c d\mathbf{u}_{c'} d\mathbf{u}_d d\gamma. \quad (21)$$

Here $\gamma = \sqrt{m_{cd}/(2kT)}g$, $\mathcal{E}_{ij}^c = \epsilon_{ij}^c/(kT)$ are the dimensionless relative velocity and internal energy. Thus from expression (8) one can easily deduce

$$v_{diss,c} k_{f,diss}^{(0)}(T) = N_A \tilde{\Omega}_{cd}^{diss(0,0)}. \quad (22)$$

Then after some transformations, taking into account that for reactions (18), (19) $v_{r,N_2} = -1$, the first order dissociation rate coefficients for N₂ can be expressed in terms of coefficients $p_{rel,c}$, ζ_c and integrals $\tilde{\Omega}_{cd}^{diss(r,p)}$:

$$k_{f,r} = k_{f,r}^{(0)} - k_{f,r}^{(1)} - k_{f,r}^{(2)}, \quad (23)$$

$$\frac{k_{f,r=1}^{(1)}}{N_A} = -\frac{p_{rel,N_2} + 2p_{rel,N}}{3p} \left[\frac{3}{2} \tilde{\Omega}_{N_2N}^{diss(0,0)} - \tilde{\Omega}_{N_2N}^{diss(1,0)} \right] + \frac{c_{tr}}{x_{N_2} c_{int,N_2}} \frac{p_{rel}}{p} \left[\tilde{\Omega}_{N_2N}^{diss(0,1)} - \langle \mathcal{E}_{ij}^c \rangle \tilde{\Omega}_{N_2N}^{diss(0,0)} \right], \quad (24)$$

$$\frac{k_{f,r=2}^{(1)}}{N_A} = -\frac{p_{rel,N_2}}{p} \left[\frac{3}{2} \tilde{\Omega}_{N_2N_2}^{diss(0,0)} - \tilde{\Omega}_{N_2N_2}^{diss(1,0)} \right] + \frac{2c_{tr}}{x_{N_2} c_{int,N_2}} \frac{p_{rel}}{p} \left[\tilde{\Omega}_{N_2N_2}^{diss(0,1)} - \langle \mathcal{E}_{ij}^c \rangle \tilde{\Omega}_{N_2N_2}^{diss(0,0)} \right], \quad (25)$$

$$\frac{k_{f,r=1}^{(2)}}{N_A} = \frac{(\zeta_{N_2} + 2\zeta_N) \nabla \cdot \mathbf{v}}{3p} \left[\frac{3}{2} \tilde{\Omega}_{N_2N}^{diss(0,0)} - \tilde{\Omega}_{N_2N}^{diss(1,0)} \right] - \frac{c_{tr}}{x_{N_2} c_{int,N_2}} \frac{\zeta \nabla \cdot \mathbf{v}}{p} \left[\tilde{\Omega}_{N_2N}^{diss(0,1)} - \langle \mathcal{E}_{ij}^c \rangle \tilde{\Omega}_{N_2N}^{diss(0,0)} \right], \quad (26)$$

$$\frac{k_{f,r=2}^{(2)}}{N_A} = \frac{\zeta_{N_2} \nabla \cdot \mathbf{v}}{p} \left[\frac{3}{2} \tilde{\Omega}_{N_2N_2}^{diss(0,0)} - \tilde{\Omega}_{N_2N_2}^{diss(1,0)} \right] - \frac{2c_{tr}}{x_{N_2} c_{int,N_2}} \frac{\zeta \nabla \cdot \mathbf{v}}{p} \left[\tilde{\Omega}_{N_2N_2}^{diss(0,1)} - \langle \mathcal{E}_{ij}^c \rangle \tilde{\Omega}_{N_2N_2}^{diss(0,0)} \right]. \quad (27)$$

In these expressions, c_{tr} is the specific heat of translational degrees of freedom of a mixture, c_{int,N_2} is the internal specific heat of N₂, $\langle \mathcal{E}_{ij}^c \rangle$ is the dimensionless internal energy averaged with the Boltzmann distribution:

$$\langle \mathcal{E}_{ij}^c \rangle = \frac{1}{Z_c^{int}} \sum_{ij} s_{ij}^c \mathcal{E}_{ij}^c \exp(-\mathcal{E}_{ij}^c).$$

Now, for rigorous calculation of the first order dissociation rate coefficients, the following steps are required:

1. Transport linear systems for scalar functions F_{cij} , G_{cij} [6] should be solved after some simplifications of the bracket integrals representing the coefficients of these systems. For this purpose, commonly used assumptions

of Mason and Monchick can be invoked, which allows one to express bracket integrals in terms of standard $\Omega_{cd}^{(r,p)}$ -integrals over cross sections of rapid processes and experimentally measured relaxation times of internal energy. Then, the transport systems can be solved numerically or, for a binary mixture, analytically. As the result, coefficients $p_{rel,c}$, ζ_c can be found.

- Integrals $\tilde{\Omega}_{cd}^{diss(r,p)}$ should be calculated on the basis of some assumptions about the dissociation cross sections. The most reliable data on the cross sections can be obtained on the basis of quasi-classical or trajectory calculations (see, for instance, [15]). These methods are rather precise but, unfortunately, extremely expensive from the computational point of view. Therefore, for rough estimations it is useful to apply simple analytical models, such as a modification of the step-like model taking into account the energy of relative motion along the center of mass line [9].

Using the proposed algorithm, one can calculate precisely the first order rate coefficients. However, some preliminary results can be obtained on the basis of simple analytical considerations. Indeed, analyzing expressions (24)–(27), one can see that the terms in the square brackets are of the same order as $k_{f,r}^{(0)}$. The terms like $c_{tr}/(x_{N_2} c_{int,N_2})$ are of the order of unit. Therefore, deviations of the first order rate coefficients from the zero order ones are represented mainly by the terms of the following type:

$$a = \frac{p_{rel}}{p}, \quad b = \frac{\zeta \nabla \cdot \mathbf{v}}{p}$$

These values can be treated as dimensionless parameters for the estimation of the first order corrections. The parameter a is usually assumed to be small [6]. This point requires however additional numerical justification and can be considered as an interesting subject for a further investigation. In the present study, we focus our attention on the parameter b , which is connected directly to the flow compressibility and non-homogeneity, and therefore can vary significantly for different flows.

In order to evaluate the parameter b , a supersonic expanding flow of a N_2/N mixture in a nozzle Scirocco PWT has been considered, with stagnation enthalpy 15 MJ/kg, stagnation pressure 5 bar. The real nozzle length is 5.366 m. Moreover, a hypothetical test case for a nozzle of 0.05366 m with the same stagnation parameters has also been studied. Rescaling the nozzle dimensions was proposed to enhance the $\nabla \cdot \mathbf{v}$ effect. Gas flow parameters have been provided by Dr. Domenic D'Ambrosio (Politecnico di Torino) [16], and then the parameter b has been estimated using the developed transport algorithm.

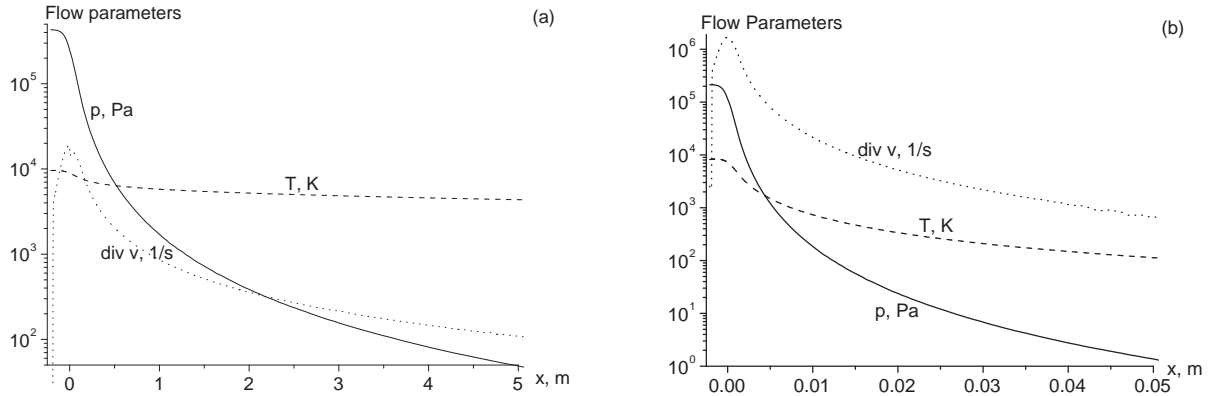


FIGURE 1. Flow parameters in a nozzle. (a): $L = 5.366$ m; (b): $L = 0.05366$ m

Fig. 1 presents flow parameters calculated for the two test cases along the nozzle axis. Rescaling the nozzle length leads to a considerable rising of the velocity divergence, whereas gas temperature and pressure change weakly. In Fig. 2, bulk viscosity coefficient ζ and parameter b are plotted as functions of x . While the behaviour of bulk viscosity is similar for both cases, parameter b increases by two orders of magnitude for the rescaled nozzle, reaching the maximum near the nozzle throat, where the values of $\nabla \cdot \mathbf{v}$ are high. Thus one can conclude that the main influence on the parameter b is due to the velocity divergence. Nevertheless, the value of the first order correction to the reaction rates remains rather small for test cases considered in this study; even for the rescaled nozzle it does not exceed 1%. One can expect a more important contribution of the first order corrections in flows with lower pressure.

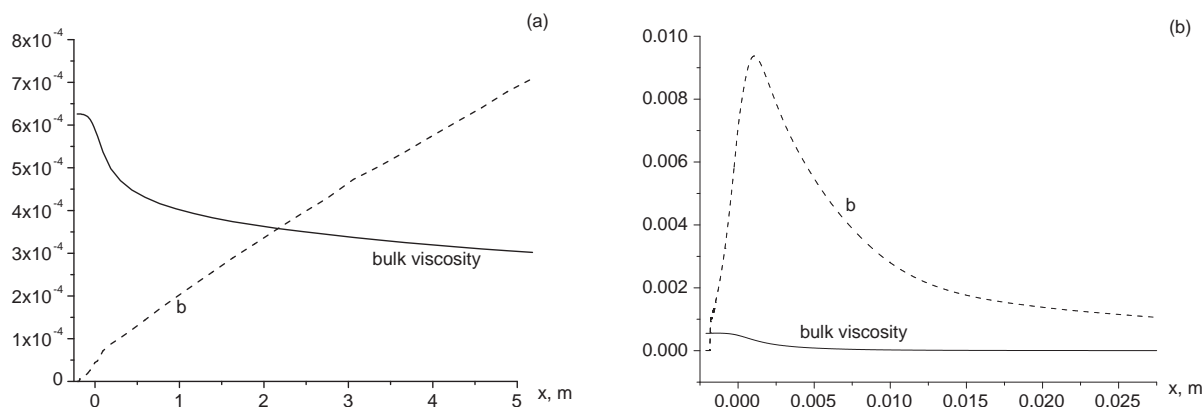


FIGURE 2. Bulk viscosity coefficient ζ , Pa·s, and parameter b . (a): $L = 5.366$ m; (b): $L = 0.05366$ m

CONCLUSIONS

First order dissociation rate coefficients are studied using the modified Chapman-Enskog method. For a binary mixture, the rate coefficients are expressed in terms of bulk viscosity coefficients, relaxation pressure, velocity divergence and collision integrals over dissociation cross sections. Dimensionless parameters useful for estimations of the first order corrections are introduced and calculated for a nozzle flow. The contribution of the first order terms is found to be weak for the conditions considered in the paper.

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