



Application of state-to-state approach in estimation of thermally nonequilibrium reaction rate constants in mode approximation

I.V. Arsentiev, B.I. Loukhovitski, A.M. Starik*

Central Institute of Aviation Motors, 111116 Moscow, Russia

ARTICLE INFO

Article history:

Available online 17 June 2011

Keywords:

Two-temperature model
Vibrational excitation
Thermally nonequilibrium kinetics
Level elementary reactions

ABSTRACT

A model to calculate nonequilibrium factor and vibrational energy lost by molecules of reagents and energy released into vibrations of product molecules in the course of chemical reactions under two-temperature approximation is suggested. The model is based on the summation of level rate constants, utilizes simple physical suppositions and does not contain any semiempirical parameters. The model demonstrates a good agreement with data on dissociation and exchange reactions obtained by using quasiclassical trajectory calculations. Then a comparison with some popular two-temperature models is performed. The developed model exhibits better versatility and coincidence with the results of QCT calculations.

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1. Introduction

For past decades a great interest was evinced in the accurate description of chemical processes in thermally nonequilibrium conditions where the vibrational and translational degrees of freedom of molecules are not equilibrated [1–17]. In general, in order to properly describe the processes, in which vibrational nonequilibrium arises, one must solve a set of master equations that govern the evolution of the population of every particular vibrational level taking into consideration both processes of vibrational relaxation and elementary reactions with molecules excited to the given vibrational states. This approach, called state-to-state, is frequently used to determine the vibrational population distribution function in model problems with reacting gas flows, when molecules have only few vibrational modes involved in a chemical reaction (mostly dissociation of diatomic molecules) [13–16]. For the analysis of more complex problems with thermally nonequilibrium phenomena in multicomponent reacting mixtures the mode approximation is widely utilized [2–11,17–19].

It was shown earlier [20] that, if vibrational relaxation is governed by vibrational–translational (V–T) and intramode vibrational–vibrational (V–V) exchanges, the population of at least lower levels of the given mode ξ even for anharmonic oscillator is governed by the Boltzmann distribution. For intermediate and high-lying levels it can deviate from the Boltzmann one and be close to the Gordiets distribution [5]. Remind, that the Treanor distribution [20] over high-lying vibrational levels is established if the rate of intramode V–V processes is much higher than that of V–T

relaxation. But we believe, that the usage of such complex types of distribution in a simplified model would not have large benefits and would lead only to loss of simplicity. For harmonic oscillator the population of all vibrational levels of the ξ th mode is Boltzmann with its own vibrational temperature T_ξ . With the supposition of an existence of vibrational temperature inside the mode one can significantly reduce the system of governing equations, because the populations of vibrational levels is described, in this case, by only one parameter. However, for any approximate model, the appropriate description of processes in reacting thermally nonequilibrium gas in terms of mode kinetics needs introducing some parameters that usually are not clearly defined and can be determined only during special investigations [21].

One can divide the whole class of thermally nonequilibrium phenomena on two groups. In the first group, the population of vibrational states of reacting molecules is greater than the equilibrium one. In terms of mode approximation, for such phenomena, the vibrational temperature T_ξ is higher than the translational temperature ($T_\xi > T$). The plasmachemical processes in electric discharge, laser-induced excitation of vibrational states of molecules, formation of vibrationally excited molecules during photodissociation of polyatomic molecules and in the course of energy chain-branching reactions are related to this group. There also exist phenomena where the population of vibrational states of initial mixture components is lower than their equilibrium population, i.e. $T_\xi < T$. Such a situation is observed behind shock wave front and upon formation of detonation wave due to delayed excitation of vibrational states of molecules. These phenomena belong to the second group.

Certainly, even an approximate model must properly describe chemical processes in both cases. Chemical reaction rate constants in thermally nonequilibrium gas, in such models, are not governed

* Corresponding author.

E-mail address: star@ciam.ru (A.M. Starik).

by the conventional Arrhenius formula and depend on both translational and vibrational temperatures. Moreover, such models must allow to calculate with high accuracy the energy released into vibrations of molecules produced in the course of chemical reactions [18,19].

Nowadays, due to rapid development of quantum-chemical approaches, which allow one to build potential energy surfaces of elementary reactions even with excited molecules, the rate constants of level reactions can be estimated on the base of quasiclassical trajectory (QCT) calculations. However, this procedure is very computationally expensive and, in addition, the accuracy of quantum chemical methods is not very high. Moreover, this way is not convenient for general purposes because one needs to perform cumbersome calculations for a large number of unstudied reactions. This is why simpler two-temperature or multi-temperature models to evaluate thermally nonequilibrium reaction rate constants are more commonly utilized [16–19].

Earlier, different two-temperature models were proposed to calculate reaction rate constants in thermally nonequilibrium gas [2–8]. However, all of them are applicable for a limited number of reaction types (usually for the dissociation reactions only), or contain adjustable parameters, or are valid only for the conditions where $T_\xi > T$ or $T_\xi < T$. This obstructs substantially their implementation in real multicomponent fluid dynamic problems with a large number of various types of reactions. Besides that, these models are not able to describe the reactions, in which reagents and products contain several vibrational modes.

It is worth noting that in recent years the other alternative macroscopic models for simple systems were developed to reproduce rate constants in strong nonequilibrium conditions [22,23]. These models, in addition to total energy conserved in a mode, treat some additional parameters, such as population of the last vibrational level when describing nonequilibrium nitrogen dissociation. These improved macroscopic models give a good agreement with results of state-to-state calculations. But one must keep in mind that this model was developed for simple N_2/N system with one dissociation reaction. To our mind, an attempt to generalize these approaches on the case of complex molecular systems with a large number of vibrationally excited species, may lead to a significant increase of the number of introduced parameters. Though, the approach itself seems to be very fruitful.

The aim of this work is to build a simple but physically based model free of these shortcomings and to verify it for different chemical reaction types.

2. Background and methodology

In the case of thermodynamic equilibrium between translational and vibrational degrees of freedom of molecules, vibrational levels are populated according to Boltzmann distribution with the translational temperature T . In nonequilibrium conditions, this distribution can be violated.

In the state-to-state approximation, molecules in various vibrational states are treated as individual species, and rate constant of elementary level chemical reaction is dependent on the vibrational energy of reacting species. As was mentioned above, in the mode approximation, reaction rate constant k depends both on vibrational T_ξ and translational T temperatures of the reagents. Commonly, the dependence $k(T, T_\xi)$ is given by the relationship [21]

$$k(T, T_\xi) = \varphi(T, T_\xi) k^0(T).$$

Here $k^0(T)$ is the thermally equilibrium reaction rate constant at $T_\xi = T$, and $\varphi(T, T_\xi)$ is the nonequilibrium factor.

Vibrational temperature of each individual mode of the reagents can be calculated by solving, for example, an equation describing time variation of mean number of vibrational quanta ε_ξ of the ξ th mode, which under infinite harmonic oscillator approximation is given by

$$\varepsilon_\xi = g_\xi (\exp(\Theta_\xi / T_\xi) - 1)^{-1}$$

and the equation itself is the following [19]

$$\frac{d\varepsilon_\xi}{dt} = Q_{VT}^\xi + Q_{VV'}^\xi + Q_{ch}^\xi. \quad (1)$$

Here Θ_ξ and T_ξ are characteristic vibrational and local vibrational temperatures of the ξ th mode, g_ξ is the multiplicity of its degeneracy, the terms Q_{VT}^ξ and $Q_{VV'}^\xi$ specify the variation of vibrational energy due to V–T relaxation and intermode V–V' exchanges. The concrete form of these terms were presented in [19]. The term Q_{ch}^ξ specifies the variation of mean number of vibrational quanta of the ξ th mode due to occurrence of chemical reactions [21]

$$Q_{ch}^\xi = \sum_{q=1}^{M_i} \frac{(\alpha_{iq}^- - \alpha_{iq}^+)}{N_i} \times \left((\chi_{q\xi}^+ - \varepsilon_\xi) R_q^+ - (\chi_{q\xi}^- - \varepsilon_\xi) R_q^- \right). \quad (2)$$

Here M_i is the number of reactions with i th molecule containing the ξ th mode, $\alpha_{iq}^{+(-)}$ are the stoichiometric coefficients of the q th reaction leading to formation (elimination) of the i th mixture component, R_q^+ and R_q^- are the q th reaction rates in forward and backward directions, $\chi_{q\xi}^{+(-)}$ are the mean numbers of vibrational quanta lost (acquired) by the molecule during its destruction (formation) in the course of the q th reaction.

In common case, the value of $\chi_{q\xi}^{+(-)}$ are governed by the equations [6,21],

$$\chi_{q\xi}^{+(-)} = \frac{E_{vq}^{+(-)}}{\Theta_\xi} \eta_{q\xi}^{+(-)},$$

$$\eta_{q\xi}^+ = \beta_{q\xi}^2 / \sum_{i=1}^{b_q} \beta_{qi}^2, \quad \eta_{q\xi}^- = \beta_{q\xi}^2 T_{q\xi}^2 / \sum_{i=1}^{b_q} \beta_{qi}^2 / \sum_{i=1}^{b_q} \beta_{qi}^2 T_{qi}^2$$

Here $E_{vq}^{+(-)}$ is the energy lost (or acquired) by the vibrational degrees of freedom of molecule eliminated (or formed) in the course of q th reaction, β_{qi} are the coefficients of expansion of the q th chemical reaction in term of normal mode coordinates, b_q is the number of modes involved in the q th reaction. For the most cases, the coefficients β_{qi} are close to unity. Thus, the value of $E_{vq}^{+(-)}$ is a crucial parameter needed to calculate the term Q_{ch}^ξ .

The Eq. (2), in essence, states that more the value of $\chi_{q\xi}^{+(-)}$ differs from mean number of vibrational quanta ε_ξ , more rapid the variation of vibrational energy accumulated in the molecule mode is.

In the case of reacting gas, the variation of vibrational energy of molecule mode in accordance with Eq. (1) can be governed mainly by the term Q_{ch}^ξ . To calculate the magnitude of Q_{ch}^ξ , one must know a mean vibrational level of the ξ th mode, from which the reaction proceeds, and a mean vibrational level at which the product molecule forms. These values can be easily obtained summing rates of energy losses in elementary level reactions or from other physical considerations. The first way seems to be preferential, because, in this case, one can obtain the vibrational energy lost by reacting molecule and the energy released into the vibrations of molecule produced in the course of reaction as well as the nonequilibrium factor from the same physical suppositions.

By no means all models proposed to calculate the nonequilibrium factor are based on the estimation of level rate constants and, thus, can not be used to calculate the amounts of energy removed from reactant molecule vibrations and energy released into vibrational degrees of freedom of product molecules in the course of chemical reaction. An example of such a model is the well known Park model [2].

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