JOURNAL OF THERMOPHYSICS AND HEAT TRANSFER
Vol. 20, No. 1, January–March 2006

Technical Notes

TECHNICAL NOTES are short manuscripts describing new developments or important results of a preliminary nature. These Notes should not exceed 2500 words (where a figure or table counts as 200 words). Following informal review by the Editors, they may be published within a few months of the date of receipt. Style requirements are the same as for regular contributions (see inside back cover).

Statistical Model for Vibration-Chemical Reaction Interaction: Extension to Gas Mixtures

N. Belouaggadia*
Hassan II University, Casablanca, Morocco
and
R. Brun†
University of Marseille,
13170 Les Pennes Mirabeau, France

Introduction

IT is well known that the chemical rate constants are strongly influenced by the vibrational distribution of reactant molecules, for example, the molecules possessing a high degree of vibrational excitation can dissociate more easily than molecules lying in low vibrational levels, at least for not too high temperatures.[1–3] Consequently, in high translation-rotation temperature flows, if the vibrational distribution is out of equilibrium and corresponds to low-vibrational temperature, the dissociation rate constants are smaller than the equilibrium Arrhenius-type constants, as it is the case behind strong shock waves. Conversely, in a low-temperature environment, like in hypersonic expansion flows in which the vibrational temperature might be high, the recombination is favored, and the high vibrational levels might be overpopulated. The influence of the chemical reactions on the vibrational populations is also important and can contribute to strong nonequilibrium distributions.

Many analyses of this coupling have been made in the past,[4] either with more or less realistic and sophisticated physico-chemical models,[5,6] or with semi-empirical methods easily usable in hypersonic computation codes.[7,8] Recently, the present authors have proposed an approach of the problem by using a generalized Chapman–Enskog method[9,10] (GCE), applied to the resolution of the Boltzmann equation governing the processes for vibrational and chemical nonequilibrium.[11] As in the classical case, this method is based on an expansion of the molecular distribution function in a series of a "small" parameter, which is the ratio of a characteristic relaxation time of a physical process and a reference flow time. However, because of the possible simultaneity of vibrational and chemical relaxation, the classical method leads to a nonunique expansion and to different formulations.[12] The GCE method, based on an asymptotic expansion, gives a unique formulation valid whatever the degree of chemical nonequilibrium might be, assuming that the "small" parameter is the ratio of the vibrational relaxation time and the reference flow time.[11] These conditions are usual in the majority of the hypersonic flows. Thus, universal formulas have been obtained for the dissociation rate constants and for the vibrational energy loss caused by dissociation, taking into account the vibrational nonequilibrium. However, the method can only give a partial description of the vibration-recombination coupling process,[11] but this coupling is generally considered as weak.[7,13]

Practical applications of the general formulas obtained by the GCE method have been developed in most characteristic nonequilibrium flows like flows behind strong shock waves, expanding flows in nozzles and hypersonic boundary layers.[11] However, they are essentially concerned with pure diatomic gases, and no generalization to gas mixtures has been provided. Thus the aim of the present paper is to extend the results of the GCE method to reacting gas mixtures like air at high temperature and to show that this method is as efficient and fruitful in these cases as for pure dissociating gases. An application to the hypersonic airflow behind strong shock waves is also presented, as a test of the model.

Generalized Chapman–Enskog Method

From a macroscopic point of view, it is well known that reacting gas flows are usually described by Navier–Stokes or Euler equations completed by chemical species conservation equations and by vibrational relaxation equations for molecular species.[14] The coupling between these last equations arises from their comparable timescales. Thus, for each component of the mixture the mass source term caused by chemical reactions $\dot{W}_C$ depends on vibrational populations and therefore on the nonequilibrium. In the same way, the vibrational energy source terms $\dot{W}_V$ are influenced by the loss, or gain, of reactant molecules.

The GCE method essentially consists in expanding the distribution function of reacting molecules (on an internal level i) in a series of a small parameter representing the ratio of a characteristic time (here the vibrational characteristic time) and a reference flow time. The method applies to nonequilibrium zones up to complete equilibrium. Truncating the expansion to the first order, a complete expression of the distribution function can be obtained, and the coupling between vibrational and chemical nonequilibrium appears at this order. Details about the method can be found in Ref. 11. Explicit expressions for $\dot{W}_C$ and $\dot{W}_V$ are thus found, so that the rate constant K_C of each reaction participating in $\dot{W}_C$ can be written:

$$K_C = X\overline{K_C} \tag{1}$$

where $\overline{K_C} = \overline{K_C}(T)$ is the rate constant of the reaction in vibrational equilibrium conditions, depending only on the translation-rotation temperature T. X is equal to

$$X = 1 + [(e_{\mathrm{VD}} - e_V)/kT][(e_V - \bar{e}_V)/\bar{e}_V] \tag{2}$$

where e_{VD} is the mean vibrational energy lost (or gained) by the considered species in the reaction, e_V and $\bar{e}_V$ respectively the vibrational energy in local conditions and in equilibrium conditions, and k is the Boltzmann constant.

Here e_{VD} must be computed with the aid of a physical vibrational model. For example, in the case of dissociation reactions, e_{VD} is equal to $0.5e_D$ (where e_D is the dissociation energy), when the harmonic oscillator model is used and when truncating the expansion of the distribution function at the zeroth order. The value of e_{VD} is in the range 0.4–$0.5e_D$ for the anharmonic oscillator model at the same

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Received 12 February 2005; revision received 23 March 2005; accepted for publication 28 March 2005.

*Assistant Professor, Faculté des Sciences Ben Msik, Mohammedia, B. P. 7955, Sidi Othman.

†Professor Emeritus, 42 Chemin des Petits Cadeneaux.

order of the distribution function.[11] At the first order, an approximate value of $0.3e_D$ can be used instead of the complete expression[11]; it is also close to the value recommended by Sharma et al.[15] Details can be found in Ref. 11. For exchange reactions, e_{VD} represents a fraction of the activation energy, also depending on the oscillator model.

In the same way, the term $\dot{W}_V$ appearing in the vibrational energy relaxation equations and caused by various reactions is proportional to $(e_V - e_{\mathrm{VD}})\dot{W}_D$ (vibrational energy loss) and to a similar term $(e_V - e_{\mathrm{VR}})\dot{W}_R$ (vibrational energy gain), with $\dot{W}_C = \dot{W}_R - \dot{W}_D$. So, these terms can be computed in the same way, taking into account the requirements caused by equilibrium conditions.

Application to Gas Mixtures

As already indicated, the method has been first applied to pure diatomic gases essentially in the dissociating regime. In situations where the recombination is preponderant (an expanding flow for example), the model can be only applied to recombination reactions involving molecular species, as for example,

$$A_2 + A + A \rightarrow A_2 + A_2 \tag{3}$$

and the reactions with only atoms cannot be described by the present model, but, in fact, this is not a major drawback, because the coupling between vibration and recombination processes is generally considered as weak.

Anyway, considering high-temperature hypersonic airflow behind a strong shock wave as a typical example of a reacting gas mixture, in a temperature range 5–15,000 K, it is usual to take into account five neutral species (N_2, O_2, O, N, NO), with 15 dissociation reactions for the molecular species and two exchange reactions for the creation of NO (Ref. 16). In a reverse way, when approaching equilibrium, 15 recombination reactions can become significant, as well as the two reverse exchange reactions. Among these 34 possible reactions, only six among the recombination reactions are not affected by the present interaction model: thus, we can consider that this model describes the essential aspects of the nonequilibrium zone behind the shock.

Computation is performed for shock Mach numbers 12 and 25 and for initial pressures corresponding to altitudes of respectively 55 and 75 km: one-dimensional Euler equations are simultaneously solved with species mass conservation and vibrational relaxation equations including the present interaction model. The relaxation equations also take into account the TV and VV transitions.[17–19] A simple fourth-order marching procedure is applied from conditions "just" behind the shock, where "shock-slip" conditions are taken into account because of strong gradients of various parameters, up to complete equilibrium.

Results and Discussion

Rate Constants

The main expected result of this analysis concerns the modification of the rate constants because of the vibrational nonequilibrium; thus, as an example, the evolution of dissociation rate constants of N_2 is represented in Fig. 1 for a shock Mach number 25, initial pressure 2.5 Pa, and initial temperature 205 K. These constants are computed from Eq. (2) and compared with their Arrhenius equilibrium values.[15] As expected, these equilibrium values decrease from the shock because of the temperature decrease in the nonequilibrium region. On the contrary, the nonequilibrium rate constant increases up to a maximum and then decreases. This behavior of course comes from the increase of the vibrational temperature from the ambient temperature just behind the shock wave; the maximum of vibrational temperature is attained before the end of the chemical relaxation, so that the computed rate constants decrease, following the temperature decrease in the chemical nonequilibrium zone.

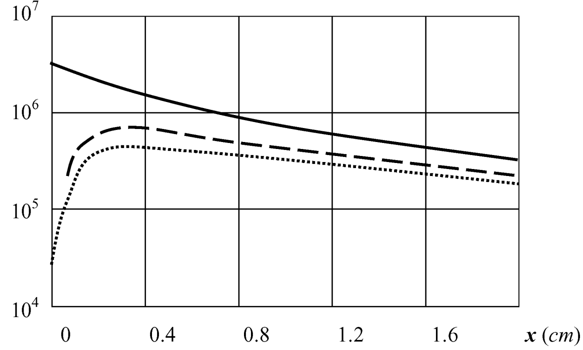

Fig. 1 Dissociation-rate constants of nitrogen behind a shock in air: ——, Arrhenius; · · · ·, Park; – – –, present model.

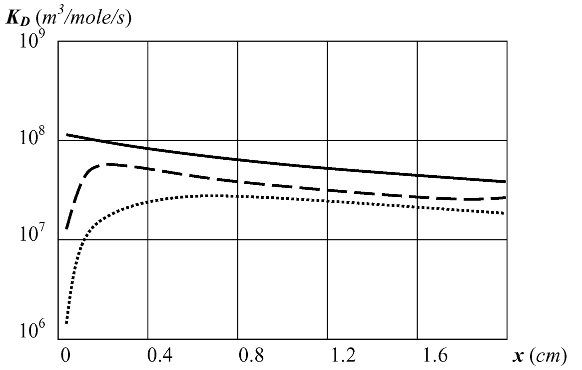

Fig. 2 Dissociation-rate constants of oxygen behind a shock in air: ——, Arrhenius; · · · ·, Park; – – –, present model.

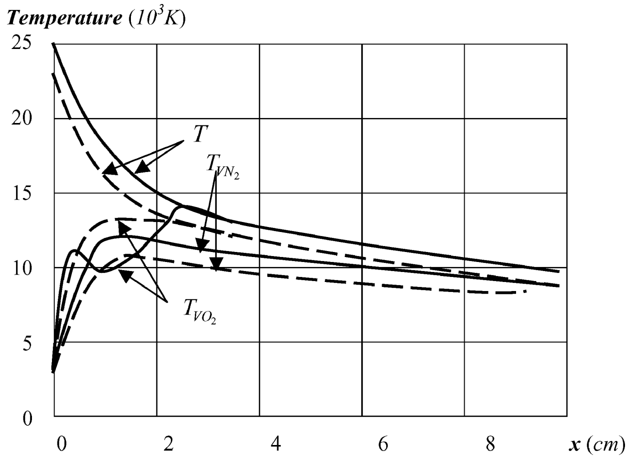

Fig. 3 Evolution of temperatures behind a shock in air: ——, with interaction; – – –, without interaction.

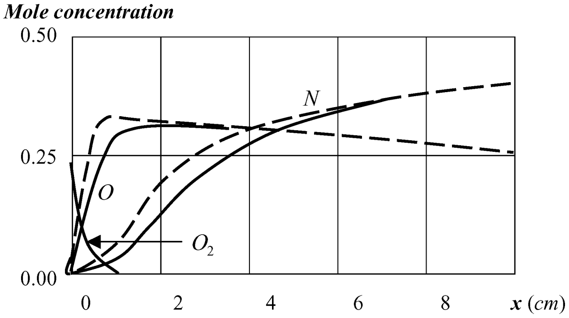

Fig. 4 Evolution of species concentrations behind a shock in air: ——, with interaction; – – –, without interaction.

The rate constants computed from Eq. (2) are also compared to those obtained from the empirical formula given by Park,[8] generally considered as realistic and widely used in hypersonic codes: Thus, in Fig. 1 (dissociation rate constants of N_2) the trend of the curves is similar, and quantitative values are close. It is the same for NO.

However, for O_2 (Fig. 2), there is a rather strong difference, probably caused by the particular behavior of the vibrational relaxation and the dissociation of O_2 (Figs. 3 and 4).

Vibrational Temperatures

The evolution of the vibrational temperatures of O_2 and N_2 is represented in Fig. 3 for the same conditions and compared with the vibrational temperatures obtained without interaction.

The first comment concerns the fact that the vibration-chemical reaction interaction contributes to lengthen the relaxation zone, and so the translational temperature decrease is more progressive. The vibrational temperature of O_2 exhibits a minimum in the nonequilibrium phase, caused by the rapid initial dissociation of oxygen molecules (see Fig. 2 of Ref. 11) followed by the efficient translation-vibration $O_2 - O$ collisions[20] quickly increasing T_{VO_2}. This minimum does not exist when the interaction is not taken into account and is not encountered in pure gases.[11] As for N_2, its vibrational temperature presents a maximum in the same phase before tending to equilibrium.

Concentrations

The lengthening of the nonequilibrium zone is clearly visible also in the evolution of the concentrations when the interaction is taken into account. In Fig. 4, the evolution of the atomic species O and N is represented, and, as expected, the dissociation is delayed because of this interaction. The dissociation of oxygen presents a maximum caused by a short vibrational relaxation zone and a subsequent temperature decrease associated with reactions involving atomic oxygen, when the concentration of N continues to increase because of the longer vibrational relaxation zone of N_2.

Conclusions

The previously established model for the interaction between vibrational relaxation and chemical reactions has been extended to gas mixtures and especially to the case of air submitted to a strong shock wave. A realistic description of the nonequilibrium zone is so obtained, which shows the interest to use this physically based model in hypersonic flow description. Other applications, notably in hypersonic boundary layers, are being considered.

Acknowledgments

The authors are particularly grateful to K. Takayama and T. Saito from Tohoku University of Sendai (Japan) for their unvaluable support and helpful discussions.

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