Study of the Reaction Rate for Reactive Binary Gaseous Mixtures

Adriano Willian da Silva

Kayk Bueno Martins

Luan Nogueira Vilkevicius

Instituto Federal do Parana, Campus Curitiba, PR, Brazil

adriano.silva@ifpr.edu.br, kaykbuenomartins@gmail.com, luan-nogueira-vilkevicius@hotmail.com

Abstract

A binary gaseous mixture with reversible reaction of type $A + A \rightleftharpoons B + B$ is studied with Boltzmann equation, assuming hard spheres cross sections for elastic collisions and step model for reactive interactions. The Chapman-Enskog method is used to obtain the solution of the Boltzmann equation in a chemical regime for which reactive interactions are of the same order as the elastic one, i.e. in the system is closed to the final stage of a chemical reaction where the affinity is considered to be a small quantity and the system tends to the chemical equilibrium. The internal degrees of freedom of the particles of the gas are not taken into account. The aim of this paper is to evaluate the approximation second of the forward reaction rate coefficient and global reaction rate. It was verified the reaction heat changes the reaction rate and these changes are great for slow activation energy..

1 Introduction

The influence of chemical reactions on the reaction rate in gas mixtures was first analyzed by Prigogine and co-works [1] using a kinetic theory based on the Boltzmann equation. Since then, several authors have studied this problem as Present [2] and Ross and Mazur [3]. The theoretical treatment of most papers involves the Chapman-Enskog method [1, 3], [4, 5]. For the reactions of the type $A + A \rightleftharpoons B + B$, which is the so-called case of symmetric reactions [6, 7], the majority of the works is concentrated on the study of the rate of reaction an its relationship with the Arrhenius formula. The deviations are more relevant for reactions with activation energy in the high altitude atmosphere, where the elastic collisions are less frequent. In the Boltzmann equation the chemical reactions are related to inelastic collisions. The value of the reaction heat distort the Maxwellian distribution function, for large values the effect becomes more important. The cross sections determining the reactive collision term can be divided into two types, namely with and without activation energy [7, 8]. The aim of this work is to analyze the influence of the reaction heat

for a binary mixture with a reversible reaction of type $A + A \rightleftharpoons B + B$ near chemical equilibrium. This kind of reaction is known as fast reactions, because the reactive processes are of the same order as the elastic ones. The Chapman-Enskog method is used to obtain the solution of the Boltzmann equation in a chemical regime for which the reactive interactions are of the same order the elastic collisions, i.e. for processes close to the beginning of the reaction where the affinity tends to zero. The resulting integral equation is solved with the expansion of the distribution function in Sonine polynomials up to first-order terms. The calculations have been performed by assuming differential hard-sphere cross sections for elastic collisions and step model for reactives interactions.

2 Boltzmann Equation

We consider a binary mixture of ideal gases whose constituents denoted by A and B, have binding energies $\varepsilon_\alpha = A, B$ and equal molecular mass m. There exist two kinds of collisions between the molecules of the gas: the elastic one which refers to non reactive interactions and the one which takes into account the reaction. The gas molecules undergo inelastic collisions with reversible reactions of the type

$$A + A \rightleftharpoons B + B. \qquad (1)$$
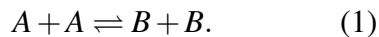
The conservation laws of linear momentum and total energy for a reactive collision are given by

$$m\mathbf{c_A} + m\mathbf{c_{A_1}} = m\mathbf{c_B} + m\mathbf{c_{B_1}}, \qquad (2)$$

$$\varepsilon_A + \frac{1}{2}mc_A^2 + \varepsilon_A + \frac{1}{2}mc_{A_1}^2 = \qquad (3)$$

$$\varepsilon_B + \frac{1}{2}mc_B^2 + \varepsilon_B + \frac{1}{2}mc_{B_1}^2,$$

where $(\mathbf{c_A}, \mathbf{c_{A_1}})$ and $(\mathbf{c_B}, \mathbf{c_{B_1}})$ are the velocities of reactants and products, respectively, of the forward reaction. The subindex 1 is used to distinguish two identical molecules that participate in the collision. The conservation laws for the nonreactive collisions have the same form as the above equations.

We denote by $\mathbf{g_A} = \mathbf{c_{A_1}} - \mathbf{c_A}$ and $\mathbf{g_B} = \mathbf{c_{B_1}} - \mathbf{c_B}$ the assymptotic relative velocities of the reactants and products of the forward reaction, respectively, and write the conservation law of total energy (3) as

$$\frac{1}{4}mg_A^2 = \frac{1}{4}mg_B^2 + E, \quad E = 2(\varepsilon_B - \varepsilon_A), \qquad (4)$$

where E, the difference between the binding energies of products and reactants is connected with the reaction heat.

In the phase space defined by positions and velocities of particles, the state of the mixture is defined in terms of the set of one-particle distribution functions

$$f_\alpha = f(\mathbf{x}, \mathbf{c}_\alpha, t) \quad (\alpha = A, B), \qquad (5)$$

such that $f_\alpha d\mathbf{x} d\mathbf{c}_\alpha$ gives at time t the number of molecules of type α in the volume element $d\mathbf{x} d\mathbf{c}_\alpha$ around the position $\mathbf{x}$ and the velocity $\mathbf{c}_\alpha$. The evolution of te one-particle distribution f_α in the phase space is assumed to satisfy the Boltzmann equation which in the absence of external forces is written as

$$\frac{\partial f_\alpha}{\partial t} + c_i^\alpha \frac{\partial f_\alpha}{\partial x_i} = Q_\alpha^E + Q_\alpha^R, \quad (\alpha = A, B) \qquad (6)$$

where

$$Q_\alpha^E = \sum_{\beta=A}^{B} \int \left[f_\alpha' f_\beta' - f_\alpha f_\beta \right] d\Gamma_{\alpha\beta}, \quad (7)$$

$$Q_\alpha^R = \int \left[f_\gamma f_{\gamma_1} - f_\alpha f_{\alpha_1} \right] \sigma_\alpha^\star d\Gamma_\alpha^\star, \quad (8)$$

where

$$d\Gamma_{\alpha\beta} = d^2 (g_{\beta\alpha}.\mathbf{k}_{\beta\alpha}) d\mathbf{k}_{\beta\alpha} d\mathbf{c}_\beta \quad (9)$$

$$d\Gamma_\alpha^\star = \sigma_\alpha^\star (\mathbf{g}_\alpha.\mathbf{k}_\alpha) d\mathbf{k}_\alpha d\mathbf{c}_{\alpha_1}$$

with the indices α and β ($\alpha \neq \beta$) representing one of the two constituents *A* and *B*, accounts for the source and sink contributions due to inelastic interactions with the chemical reactions. The quantity $\sigma_\alpha^\star$ denote reactive differential cross section, $\mathbf{k}_\alpha$ and $d\mathbf{k}_\alpha$ denote the unit collision vector and the element of solid angle for elastic collisions, whereas $\mathbf{k}_\alpha$ and $d\mathbf{k}_\alpha$ represent the corresponding quantities or reactive interactions. The parameter *d* denotes the diameter of a particle. Due to the principle of microscopic reversibility [9], a definite relationship exists between the forward cross section $\sigma_A^\star$ and that for the reverse reaction $\sigma_B^\star$. By using this principle, the transformation law bettween the elements for the reactive and forward collisions in the velocity space is given by

$$(\mathbf{g}_A.\mathbf{k}_A)\sigma_A^\star d\mathbf{c}_A d\mathbf{c}_{A_1} = (\mathbf{g}_B.\mathbf{k}_B)\sigma_B^\star d\mathbf{c}_B d\mathbf{c}_{B_1}.$$
$$(10)$$

3 Chapman-Enskog Method

The non-equilibrium effect are contained in the one-particle distribution functions, f_α, $\alpha = A, B$ and it is characterized after solving the appropriate reactive Boltzmann equation (6). This can be achieved

in the framework of the Chapman-Enskog method [1, 2], once step model for the reactive cross sections is assumed,

$$\sigma_\alpha^\star = 0, \quad \varepsilon_\alpha < \varepsilon^\star \quad or \quad d^2 \quad \gamma_\alpha > \varepsilon^\star$$
$$(11)$$

In equation (11) γ_α is the relative translational energy of constituent α and $\varepsilon^\star$ is the activation energies of the reaction in units of the thermal energy of the mixture, kT, T is the temperature of the mixture and k being the Boltzmann constant.

If we multiply the Boltzmann equation (6) by arbitrary function $\psi_\alpha = 1, \psi_\alpha = mc_i^\alpha$ and $\psi_\alpha = mc_\alpha^2/2 + \varepsilon_\alpha$, respectively and integrate the resulting equations over all values of $\mathbf{c}_\alpha$, we get the equations

$$\frac{\partial n_\alpha}{\partial t} + \frac{\partial}{\partial t}(n_\alpha v_i + n_\alpha u_i^\alpha) = \quad (12)$$

$$\int (Q_\alpha^E + Q_\alpha^R) d\mathbf{c}_\alpha = \tau_\alpha,$$

$$\frac{\partial}{\partial t}(mn_\alpha)v_i^\alpha + \frac{\partial}{\partial x_j}[p_{ij}^\alpha + mn_\alpha(u_i^\alpha v_j \quad (13)$$

$$+u_j^\alpha v_i + v_i v_j)] = \int mc_i^\alpha (Q_\alpha^E + Q_\alpha^R) d\mathbf{c}_\alpha,$$

$$\frac{\partial}{\partial t}\left[\frac{3}{2} n_\alpha kT + n_\alpha \varepsilon_\alpha + mn_\alpha \left(u_i^\alpha v_i + \frac{1}{2}v^2 \right) \right] +$$
$$(14)$$

$$\frac{\partial}{\partial x_i}\left\{ q_i^\alpha + p_{ij}^\alpha v_j + n_\alpha \varepsilon_\alpha u_i^\alpha + \right.$$

$$\frac{1}{2}mn_\alpha v^2 u_i^\alpha + \left[\frac{3}{2}n_\alpha kT + n_\alpha \varepsilon_\alpha + \right.$$

$$\left. mn_\alpha \left(u_i^\alpha v_i + \frac{1}{2}v^2 \right) \right] v_i \right\} =$$

$$= \int \left(\frac{m}{2}c_\alpha^2 \right)(Q_\alpha^E + Q_\alpha^R) d\mathbf{c}_\alpha,$$

where n_α is particle densities, v_i^α is the velocity components, T is the temperature of the mixture, u_i^α is the diffusion velocity, p_{ij}^α is pressure tensor, q_i^α is the heat flux for each constituent α and τ_α denotes the rate of reaction due to the chemical reaction. The quantities above are defined in terms of the distribution function [5].

The distribution function contains all the information about the non-equilibrium effects induced by the chemical reaction. The solution of the Boltzmann equation (6) in a chemical regime for which the reaction process is close to its final stage (fast process) to this problem is based on the Chapman-Enskog method and Sonine polynomial approximation to the coefficients of the distribution functions [10].

For the solution of the Boltzmann equation (6) it is convenient to write f_α in terms of Sonine polynomials and retain, at least, the expansion up to the first-order term,

$$f_\alpha = f_\alpha^M \left[1 + a_0^\alpha + a_1^\alpha \left(\frac{3}{2} - \frac{m\xi_\alpha^2}{2kT} \right) \right],$$
(15)
$$f_\alpha^M = n_\alpha \left(\frac{m}{2\pi kT} \right)^{3/2} exp \left(-\frac{m\xi_\alpha^2}{2kT} \right)$$

where a_1^α is scalar coefficient to be determined and $a_0^\alpha = 0$, due to particle number densities conservation of the system. The expansion adopted is capable to reproduce an appreciate effect of the reaction heat and reactive cross section on the distribution function.

4 Results

The rate of reaction of the mixture is defined by

$$\tau_\alpha = \int \left[f_\gamma f_{\gamma_1} - f_\alpha f_{\alpha_1} \right] d\Gamma_\alpha^\star d\mathbf{c}_\alpha, \quad (16)$$

When the reaction is forward ($A + A \rightarrow B + B$), the rate of reaction is

$$\tau_A = n_B^2 [k_r^{(0)} + k_r^{(1)}] - n_A^2 [k_f^{(0)} + k_f^{(1)}] \quad (17)$$

The production terms $k_f^{(0)}$, $k_f^{(1)}$, $k_r^{(0)}$ and $k_r^{(1)}$ of the particle number density can be calculated by inserting the distribution (16) into its definition (17) and by integration over all velocities $\mathbf{c}_\alpha$. The terms $k_f^{(0)}$ and $k_r^{(0)}$ are well known in the literature [8].
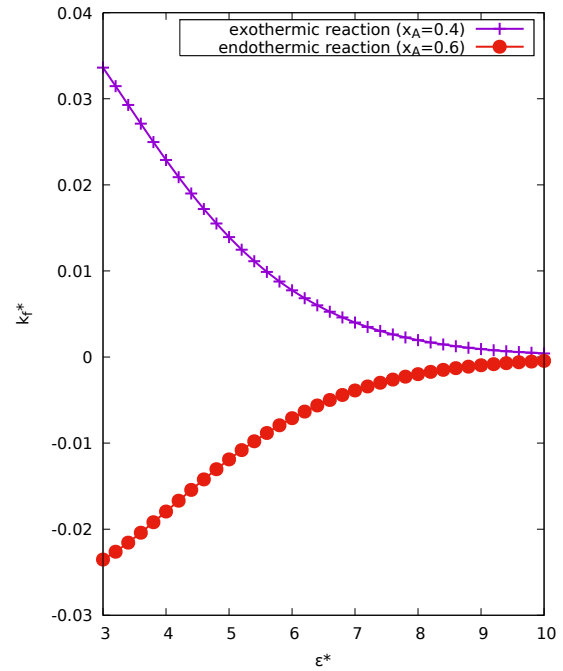

Figure 1: Dimensionless Forward Reaction Rate Coefficient as a function of the activation energy $\varepsilon^\star$ with exothermic reaction and endothermic reaction

In figures 1 and 2 are plotted respectively, the dimensionless forward reaction rate coefficient $k_f^\star$ and rate of reaction is defined by

$$k_f^\star = \frac{k_f^{(1)}}{4dr^2 \sqrt{\pi kT/m}(\varepsilon^\star + 1)e^{-\varepsilon^\star}}, \quad (18)$$

$$\tau_A^\star = \frac{\tau_A^{(1)}}{4dr^2\sqrt{\pi kT/m}(\varepsilon^\star+1)e^{-\varepsilon^\star}} \quad (19)$$

as a function of the $\varepsilon^\star$, considering the diameter $dr = d$. Two cases are analyzed, one for endothermic reaction and other for exothermic reaction.
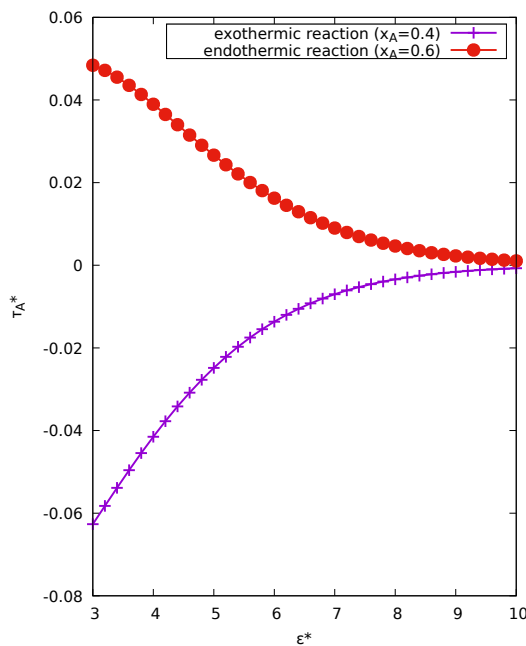

Figure 2: Dimensionless Rate of Reaction as a function of the activation energy $\varepsilon^\star$

with endothermic reaction and exothermic reaction

From figure 1 we can conclude that the effect on the reaction rate is larger exothermic reactions. Besides, the effect on the reaction rate is more evident in regions of low activation energy. As it was pointed out by Prigogine and Mahieu [1] the reaction heat modifies the distribution function.

On the other hand, in the figures 1 and 2, when the activation energy increase the rate of reaction tends to zero, the reactive cross section decreases and therefore it is less suitable to happen a collision that causes a chemical reaction.

The rate of reaction is positive for endothermic reactions and negative for exothermic reactions. Therefore, the reaction of heat modifies the distribution function.

5   Conclusions

In this paper, the second approximation to the distribution functions were determined from the system of Boltzmann equations for the last stage of a chemical reaction- known as fast reaction- where the affinity is considered as a small quantity in comparison with the thermal energy of the mixture. The reaction heat modifies the reaction rate, i. e., the production term $\tau - A$ of the particle number density of the constituent A are negative for exothermic reactions and positive for endothermic ones. It is shown the reaction to occur only when the relative translational energy is greater than the activation energy.

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