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Analysis of the Rate of Reaction for Quaternary Gaseous Mixtures near the Chemical Equilibrium

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Abstract: *A quaternary gaseous mixture with reversible reaction of type $A + B \rightleftharpoons C + D$ is studied with Boltzmann equation, assuming hard spheres cross sections for elastic collisions and the line-of-center to reactive collisions. 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 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 reaction rate coefficient of the mixture and global reaction rate. It was verified by some factors- the concentration of the reagents, the mass and diameter of the particles, the activation energy and the heat of reaction. Theses factors changes the reaction rate and the modifications are great for small values of the activation energy for reactive interactions.*
keyword: quaternary mixture, Boltzmann, reactive rate

1. INTRODUCTION

We study in this work mixture composed by four constituents whose molecules are interacting by means of elastic collisions and also by means of bimolecular reactions. The analysis of chemical reactions within the framework of Boltzmann equation is an old subject in the literature dating back to the middle of the last century with the publication of the pioneer work by Prigogine and Xrhouet (1). After these seminal work, several papers appear in the literature concerning the study of the Boltzmann equation applied to chemical processes and among others we quote the works of Present (2), Ross and Mazur (3), Shizgal and Karplus (4), Cukrowski and Popielawski (5). In this paper we present a kinetic theory for a four constituent gas mixture which undegoes a binary and reversible chemical reactions of the type $A + B \rightleftharpoons -C + D$. The gas mixture under examination is composed by monatomic ideal gases or, i. e., the internal degrees of freedom of the molecules- like rotational and vibrational modes- are not taken into account. This simplification enables us to determine analytically the collision integrals of the Boltzmann equation by considering a rigid spheres model fo the elastic cross section and a line-of-center energy model for the reactive cross section. We have also considered that the gas mixture is close to the chemical equilibrium. This kind of reaction is known as fast reactions, because the reactive processes are of the same order as the elastic ones, i.e, the affinity is considered as a small quantity in comparison with the thermal energy of the mixture. For this reason the affinity is also considered a thermodynamical force. 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. The resulting integral equation is solved with the expansion of the distribution function in Sonine polynomials up to first-order terms.

2. BOLTZMANN EQUATION AND BALANCE EQUATIONS

We consider a mixture of ideal gases of four constituents A, B, C e D unergoing a simple reversible bimolecular reaction of the type $A + B \rightleftharpoons C + D$. 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 conservation laws of linear momentum and total energy for a reactive collision are given by

$$m_A + m_B = m_C + m_D \tag{1}$$

$$m_A \mathbf{c_A} + m_B \mathbf{c_B} = m_C \mathbf{c_C} + m_D \mathbf{c_D}, \tag{2}$$

$$\epsilon_A + \frac{1}{2}m_A c_A^2 + \epsilon_B + \frac{1}{2}m_B c_B^2 = \epsilon_C + \frac{1}{2}m_C c_B^2 + \epsilon_D + \frac{1}{2}m_D c_D^2, \tag{3}$$

where ($\mathbf{c_A}$, $\mathbf{c_B}$) and ($\mathbf{c_C}$, $\mathbf{c_D}$) are the velocities of reactants and products, respectively, of the forward reaction. The conservation laws for the elastics collisions have the same form as the above equations.

We denote by $\mathbf{g_{BA}} = \mathbf{c_B} - \mathbf{c_A}$ and $\mathbf{g_{DC}} = \mathbf{c_D} - \mathbf{c_C}$ the assymptotic relative velocities of the reactants and products of the forward reaction, respectively, and write the conservation law of total energy (3) as

$$\frac{1}{2}m_{AB}g_{BA}^2 = \frac{1}{2}m_{CD}g_{CD}^2 + E, \qquad E = \epsilon_D + \epsilon_C - \epsilon_B - \epsilon_A, \tag{4}$$

where E, the difference between the binding energies of products and reactants is connected with the reaction heat and $m_{\alpha\beta} = m_\alpha m_\beta/(m_\alpha + m_\beta)$, where $\alpha = A, B, C, D$ and $\beta = A, B, C, D$.

The affinity $\mathcal{A}$ for the forward reaction is defined by (10)

$$\mathcal{A} = kTln\left(\frac{n_A n_B n_C^{eq} n_D^{eq}}{n_C n_D n_A^{eq} n_B^{eq}}\right), \tag{5}$$

where it vanishes for equilibrium processes.

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

$$f_\alpha = f(\mathbf{x}, \mathbf{c}_\alpha, t) \qquad (\alpha = A, B, C, D), \tag{6}$$

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

$$\frac{\partial f_\alpha}{\partial t} + c_i^\alpha \frac{\partial f_\alpha}{\partial x_i} = Q_\alpha^E + Q_\alpha^R, \qquad (\alpha = A, B, C, D) \tag{7}$$

where

$$Q_\alpha^E = \sum_{\beta=A}^{D} \int \left[f'_\alpha f'_\beta - f_\alpha f_\beta\right] d\Gamma_{\alpha\beta}, \tag{8}$$

$$Q_{AB}^R = \int \left[f_C f_D \left(\frac{m_{AB}}{m_{CD}}\right)^3 - f_A f_B\right] \sigma_{AB}^\star d\Gamma_{AB}^\star,$$

$$Q_{CD}^R = \int \left[f_A f_B \left(\frac{m_{CD}}{m_{AB}}\right)^3 - f_C f_D\right] \sigma_{CD}^\star d\Gamma_{CD}^\star \tag{9}$$

and

$$d\Gamma_{\alpha\beta} = d^2(\mathbf{g}_{\beta\alpha}.\mathbf{k}_{\beta\alpha}) d\mathbf{k}_{\beta\alpha} d\mathbf{c}_\beta \tag{10}$$

$$d\Gamma_{AB}^\star = \sigma_{AB}^\star (\mathbf{g}_{BA}.\mathbf{k}_{BA}) d\mathbf{k}_{BA} d\mathbf{c}_B,$$

$$d\Gamma_{CD}^\star = \sigma_{CD}^\star (\mathbf{g}_{DC}.\mathbf{k}_{DC}) d\mathbf{k}_{DC} d\mathbf{c}_D \tag{11}$$

with the indexes α and β ($\alpha \neq \beta$) representing one of the four constituents A, B, C and D. The quantities $\sigma_{BA}^\star$ and $\sigma_{DC}^\star$ 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 (8), a definite relationship exists between the forward cross section $\sigma_{BA}^\star$ and that for the reverse reaction $\sigma_{DC}^\star$. By using this principle, the transformation law between the elements for the reactive and forward collisions in the velocity space are given by

$$m_{CD} g_{BA} d\mathbf{k}_{BA} d\mathbf{c}_C d\mathbf{c}_D = m_{AB} g_{DC} d\mathbf{k}_{DC} d\mathbf{c}_A d\mathbf{c}_B$$

$$m_{CD}^2 g_{DC}^2 \sigma_{CD}^\star = m_{AB}^2 g_{BA}^2 \sigma_{AB}^\star. \tag{12}$$

3. CHAPMAN-ENSKOG METHOD

In order to obtain the reactive rate of a four constituent gas mixture we consider that the system is nearby a chemical equilibrium state, so that the frequencies of chemical reactions- which are related to non elastic collisions- have the same order as the frequencies of elastic collisions. The non-equilibrium effect are contained in the one-particle distribution functions, f_α, $\alpha = A, B, C, D$ 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). The reactive cross section used in this work is the line-of-center energy model proposed by Present (2)

$$\sigma_\alpha^\star = 0, \quad \varepsilon_\alpha < \varepsilon^\star \quad or \quad dr^2\left(1 - \frac{\varepsilon^\star}{\gamma_\alpha}\right), \quad \gamma_\alpha > \varepsilon^\star \tag{13}$$

In equation above 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, i.e., for line-of-center model

$$\gamma_\alpha = \frac{mg_\alpha^2}{4kT}, \quad \varepsilon_A^\star = \frac{\varepsilon_A}{kT}, \quad \varepsilon_B^\star = \varepsilon_A^\star - E^\star, \quad E^\star = \frac{E}{kT}. \tag{14}$$

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 termal 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 $\psi_\alpha = 1$,$\psi_\alpha = m_\alpha c_i^\alpha$ and $\psi_\alpha = mc_\alpha^2/2 + \epsilon_\alpha$, respectively and integrate the resulting equations over all values of $\mathbf{c}_\alpha$, we get the equations

$$\frac{\partial n_\alpha}{\partial t} + \frac{\partial}{\partial t}(n_\alpha v_i + n_\alpha u_i^\alpha) = \int (Q_\alpha^E + Q_\alpha^R) d\mathbf{c}_\alpha = \tau_\alpha, \tag{15}$$

$$\frac{\partial}{\partial t}(mn_\alpha)v_i^\alpha + \frac{\partial}{\partial x_j}[p_{ij}^\alpha + mn_\alpha(u_i^\alpha v_j + u_j^\alpha v_i + v_i v_j)] = \int m_{c_i}{}^\alpha (Q_\alpha^E + Q_\alpha^R) d\mathbf{c}_\alpha, \tag{16}$$

$$\frac{\partial}{\partial t}\left[\frac{3}{2}n_\alpha kT + n_\alpha \epsilon_\alpha + mn_\alpha\left(u_i^\alpha v_i + \frac{1}{2}v^2\right)\right] + \frac{\partial}{\partial x_i}\left\{q_i^\alpha + p_{ij}^\alpha v_j + n_\alpha \epsilon_\alpha u_i^\alpha + \frac{1}{2}m_\alpha n_\alpha v^2 u_i^\alpha\right.$$

$$\left. + \left[\frac{3}{2}n_\alpha kT + n_\alpha \epsilon_\alpha + m_\alpha n_\alpha\left(u_i^\alpha v_i + \frac{1}{2}v^2\right)\right] v_i\right\} = \int \left(\frac{m_\alpha}{2}c_\alpha^2\right)(Q_\alpha^E + Q_\alpha^R) d\mathbf{c}_\alpha, \tag{17}$$

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 (11).

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 (9).

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,

$$f_\alpha = f_\alpha^M\left\{1 + \left[e_0^\alpha + e_1^\alpha\left(\frac{3}{2} - \frac{m\xi_\alpha^2}{2kT}\right)\right]\right\},$$

$$f_\alpha^M = n_\alpha\left(\frac{m_\alpha}{2\pi kT}\right)^{3/2} exp\left(-\frac{m_\alpha \xi_\alpha^2}{2kT}\right) \tag{18}$$

where e_0^α and e_1^α are scalar coefficients to be determined. The expansion adopted is capable to reproduce an appreciate effect of the reaction heat and reactive cross section on the distribution function and consequently on the reaction rate.

4. RESULTS

The reaction rate for quaternary gaseous mixture is defined by

$$\tau_A = \tau_B = \int \left[f_C f_D\left(\frac{m_{AB}}{m_{CD}}\right)^3 - f_A f_B\right] \sigma_{AB}^\star d\Gamma_{AB}^\star d\mathbf{c}_A$$

$$\tau_C = \tau_D = \int \left[f_A f_B\left(\frac{m_{CD}}{m_{AB}}\right)^3 - f_C f_D\right] \sigma_{CD}^\star d\Gamma_{CD}^\star d\mathbf{c}_C \tag{19}$$

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

$$\tau_A = n_C n_D[k_r^{(0)} + k_r^{(1)}] - n_A n_B[k_f^{(0)} + k_f^{(1)}] \tag{20}$$

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 (7).

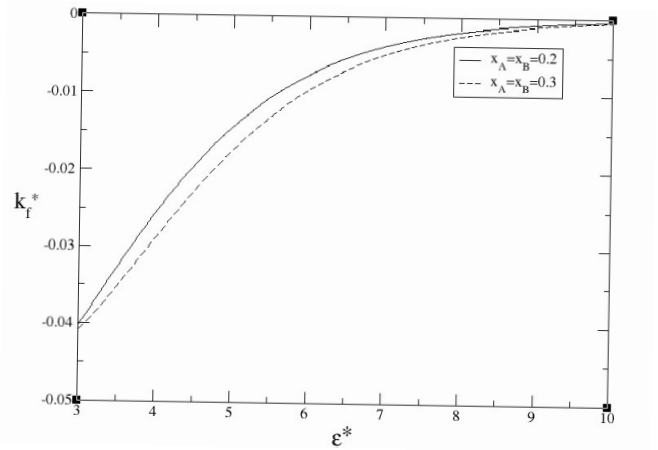

Figura 1: Dimensionless Forward Reactive Rate Coefficient as a function of the activation energy $\varepsilon^\star$ with $m_A = m_C = 2m$ and $m_B = m_D = m$ and $d_A = d_B = d_C = d_D = d$

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

$$k_f^\star = \frac{k_f^{(1)}}{2dr^2\sqrt{\pi kT/m_{AB}}(\varepsilon^\star + 1)e^{-\varepsilon^\star}}, \tag{21}$$

$$\tau_A^\star = \frac{\tau_A^{(1)}}{2dr^2\sqrt{\pi kT/m_{AB}}(\varepsilon^\star + 1)e^{-\varepsilon^\star}} \tag{22}$$

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.

In both the cases, endothermic and exothermic reactions, the reactive diameter of the molecules is $dr = d$.

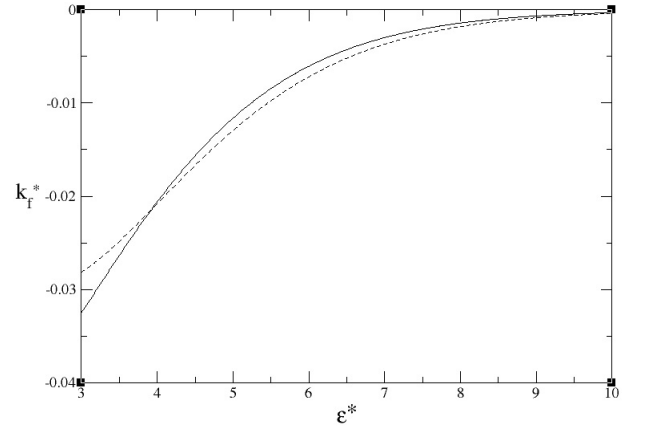

Figura 2: Dimensionless Forward Reactive Rate Coefficient as a function of the activation energy $\varepsilon^\star$ with $m_A = m_C = 3m$ and $m_B = m_D = m$ and $d_A = d_B = d_C = d_D = d$

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 big for endothermic reactions than for exothermic reactions. Therefore, the reaction of heat modifies the distribution function. Besides the rate of reaction is small to molecules more massive.

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.The results concerning the influence of chemical reactions on the transport coefficient obtained here are general since here we have used the complete collision term of the Boltzmann equation.

6. ACKNOWLEDGMENTS

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8. RESPONSABILIDADE AUTORAIS

Os autores são únicos responsáveis pelo conteúdo deste trabalho.