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THE EFFECTS OF THE CROSS SECTION ON THE DIFFUSION COEFFICIENT OF BINARY GASEOUS MIXTURES

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Abstract: *The effects caused by the cross section on the reaction rate of a binary mixture of ideal gases which undergo a simple reversible symmetric reaction of the type $A+A \rightleftharpoons B+B$ are analyzed from the Boltzmann equation. The system is analyzed to a general case of the stage of chemical reaction and to the final stage of a chemical reaction where the systems tends of a chemical equilibrium. This stage the a reaction is known as fast reactions, because the reactive processes are of the same order as the elastics. The binary mixture is examined with a Champman-Enskog method and internal degrees of freedom of the particles of the gas are not considered into the account. The main objectives are to study the effect of the Present cross section and modified Present cross section in the diffusion coefficient of the gases mixture. It was verified by some factors- the concentration of the reagents, the activation energy and the heat of reaction. These factors change the diffusion coefficient of the reactive gases mixture and the modifications are great for small values of the activation energy and to Present reactive cross section .*

Keywords: binary mixture, diffusion coefficient, reactive cross section

1. INTODUCTION

The analysis of chemical reactions within the framework of Boltzmann equation is an old subject in the literature dating back to the middle of last century with the publication of the pioneer work by Prigogine and Xrhouet (1). After these seminal work, several papers appeared in the literature concerning the study of the Boltzmann equation applied to chemical processes and among others that were quoted in the works of Present (2), Ross and Mazur (3), Shizgal and Karplus (4), Cukrowski and Popielawski (5). For the reactions of the type $A + A \rightleftharpoons B + B$, which is the case so-called case of symmetric reactions (5), the majority of the works are concentrated on the study concerning rate of reaction and 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 determines the reactive collision term can be divided into two types, namely with and without activation energy (6; 7). The aim of this work is to study the influence of the reaction heat in the diffusion coefficient 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, i.e, the affinity is considered as a small quantity in comparison with the thermal energy of the mixture. 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. The calculations have been performed by assuming differential hard-sphere cross sections for elastic collisions, line-of-centers and modified line-of-centers models for reactives interactions.

2. BOLTZMANN EQUATION

A simple reversible reaction is characterized by a binary mixture of ideal gases whose constituents denoted by A and B undergo a reaction of the type $A + A \rightleftharpoons B + B$. The molecules of the constituents have equal masses $m_A = m_B = m$ and the formation or binding energy are denoted by $\epsilon_\alpha = A, B$. 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

$$m\mathbf{c_A} + m\mathbf{c_{A_1}} = m\mathbf{c_B} + m\mathbf{c_{B_1}}, \tag{1}$$

$$\epsilon_A + \frac{1}{2}mc_A^2 + \epsilon_A + \frac{1}{2}mc_{A_1}^2 = \epsilon_B + \frac{1}{2}mc_B^2 + \epsilon_B + \frac{1}{2}mc_{B_1}^2, \tag{2}$$

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 elastics 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

$$\frac{1}{4}mg_A^2 = \frac{1}{4}mg_B^2 + E, \qquad E = 2(\epsilon_B - \epsilon_A), \tag{3}$$

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

$$f_\alpha = f(\mathbf{x}, \mathbf{c}_\alpha, t) \qquad (\alpha = A, B), \tag{4}$$

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 the 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

$$\frac{\partial f_\alpha}{\partial t} + c_i^\alpha \frac{\partial f_\alpha}{\partial x_i} = Q_\alpha^E + Q_\alpha^R, \qquad (\alpha = A, B) \tag{5}$$

where

$$Q_\alpha^E = \sum_{\beta=A}^{B} \int \left[f'_\alpha f'_\beta - f_\alpha f_\beta\right] d\Gamma_{\alpha\beta}, \tag{6}$$

$$Q_\alpha^R = \int \left[f_\gamma f_{\gamma_1} - f_\alpha f_{\alpha_1}\right] \sigma_\alpha^\star d\Gamma_\alpha^\star, \tag{7}$$

and

$$\begin{aligned} d\Gamma_{\alpha\beta} &= d^2(g_{\beta\alpha}.\mathbf{k}_{\beta\alpha})d\mathbf{k}_{\beta\alpha}d\mathbf{c}_\beta \\ d\Gamma_\alpha^\star &= \sigma_\alpha^\star(\mathbf{g}_\alpha.\mathbf{k}_\alpha)d\mathbf{k}_\alpha d\mathbf{c}_{\alpha_1} \end{aligned} \tag{8}$$

with the indices α and β ($\alpha \neq \beta$) represent 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 $\sigma_\alpha^\star$ denotes 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 definitive 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 between the elements for the reactive and forward collisions in the velocity space is given by

$$(\mathbf{g}_A.\mathbf{k}_A)\sigma_A^\star d\mathbf{c}_A d\mathbf{c}_{A_1} = (\mathbf{g}_B.\mathbf{k}_B)\sigma_B^\star d\mathbf{c}_B d\mathbf{c}_{B_1}. \tag{9}$$

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). The models of the reactive cross section used int this paper are the line-of-centers model and modified line-of-centers,

$$\sigma_\alpha^\star = 0, \quad \varepsilon_\alpha < \varepsilon^\star \quad or \quad dr^2\left(1 - \frac{\varepsilon^\star}{\gamma_\alpha}\right), \quad \gamma_\alpha > \varepsilon^\star \tag{10}$$

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-centers model

$$\gamma_\alpha = \frac{mg_\alpha^2}{4kT}, \qquad \varepsilon_A^\star = \frac{\varepsilon_A}{kT}, \qquad \varepsilon_B^\star = \varepsilon_A^\star - E^\star, \qquad E^\star = \frac{E}{kT}. \tag{11}$$

While for modified line-of-centers model

$$\gamma_\alpha = \frac{m(\mathbf{g}_\alpha.\mathbf{k}_\alpha)^2}{4kT} \tag{12}$$

In equation (11) γ_α is the relative translational energy of constituent α and $\varepsilon^\star$ is the activation energy 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 $\psi_\alpha = 1$,$\psi_\alpha = mc_i^\alpha$ 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

$$\frac{\partial n_\alpha}{\partial t} + \frac{\partial}{\partial t}(n_\alpha v_i + n_\alpha u_i^\alpha) = \int (Q_\alpha^E + Q_\alpha^R) d\mathbf{c}_\alpha = \tau_\alpha, \tag{13}$$

$$\frac{\partial}{\partial t}(mn_\alpha)v_i^\alpha + \frac{\partial}{\partial x_j}[p_{ij}^\alpha + mn_\alpha(u_i^\alpha v_j + u_j^\alpha v_i + v_i v_j)] = \int mc_i^\alpha (Q_\alpha^E + Q_\alpha^R) d\mathbf{c}_\alpha, \tag{14}$$

$$\begin{aligned}&\frac{\partial}{\partial t}\left[\frac{3}{2}n_\alpha kT + n_\alpha \epsilon_\alpha + mn_\alpha\left(u_i^\alpha v_i + \frac{1}{2}v^2\right)\right] + \frac{\partial}{\partial x_i}\left\{q_i^\alpha + p_{ij}^\alpha v_j + n_\alpha \epsilon_\alpha u_i^\alpha + \frac{1}{2}mn_\alpha v^2 u_i^\alpha + \right.\\ &\left.\left[\frac{3}{2}n_\alpha kT + n_\alpha \epsilon_\alpha + mn_\alpha\left(u_i^\alpha v_i + \frac{1}{2}v^2\right)\right] v_i\right\} = \int \left(\frac{m}{2}c_\alpha^2\right)(Q_\alpha^E + Q_\alpha^R) d\mathbf{c}_\alpha,\end{aligned} \tag{15}$$

where n_α is the 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 the 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 (10).

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,

$$\begin{aligned}&f_\alpha = f_\alpha^M\left[1 + d_0^\alpha \xi_i^\alpha\right],\\ &f_\alpha^M = n_\alpha\left(\frac{m}{2\pi kT}\right)^{3/2} exp\left(-\frac{m\xi_\alpha^2}{2kT}\right)\end{aligned} \tag{16}$$

where d_0^α is scalar coefficient 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 diffusion coefficient.

The diffusion velocity of constituent A is defined by

$$u_i^A = \frac{1}{n_A}\int \xi_i^A f_A d\mathbf{c_A} \tag{17}$$

The balance equation for the partial particle number density n_B of the constituent B leads $u_i^B = -n_A u_i^A/n_B$, because it is one independent diffusion velocity for the mixture.

4. RESULTS

The diffusion velocity of the mixture is defined by equation 17 and it can to be write by

$$u_i^A = -\frac{D_{12}}{x_A}d_i^A, \ with \ D_{12} = x_A\frac{kT}{m}d_0^A \tag{18}$$

The coefficient D_{12} is called diffusion coefficient. The mass flux is direct effect when your source is related diffusion force.

In figures 1 and 2 are plotted respectively, the dimensionless diffusion coefficient $D^\star$ is defined by

$$D^\star = \frac{D_{12}}{D_{11}}, \tag{19}$$

where

$$D_{11} = \frac{177}{464}\frac{1}{nd^2}\left(\frac{kT}{\Pi m}\right)^{1/2} \tag{20}$$

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

From figure 1 we can conclude that the effect on the diffusion coefficient is larger for line-of-center model and endothermic reactions than for modified line-of-center model and exothermic reactions. Besides, the effect on the diffusion coefficient 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 increases the diffusion coefficient of the reaction tends to one, the reactive cross section decreases and therefore it is less probable to happen a collision that causes a chemical reaction.

The diffusion coefficient is larger for endothermic reactions and small for exothermic reactions. Therefore, the reaction of heat modifies the distribution function.

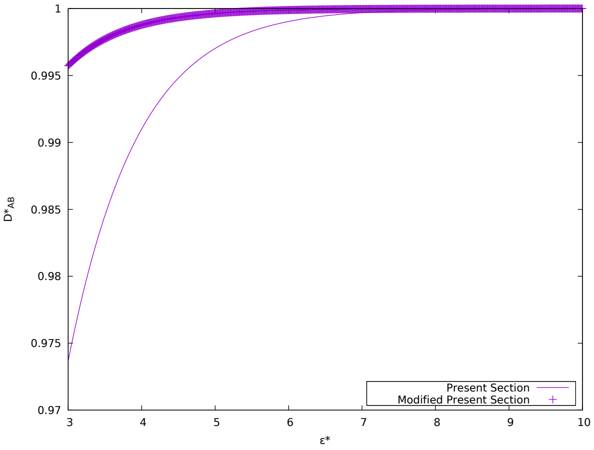

Figura 1: Dimensionless Diffusion Coefficient as a function of the activation energy $\varepsilon^\star$ with $x_A = 0.4$

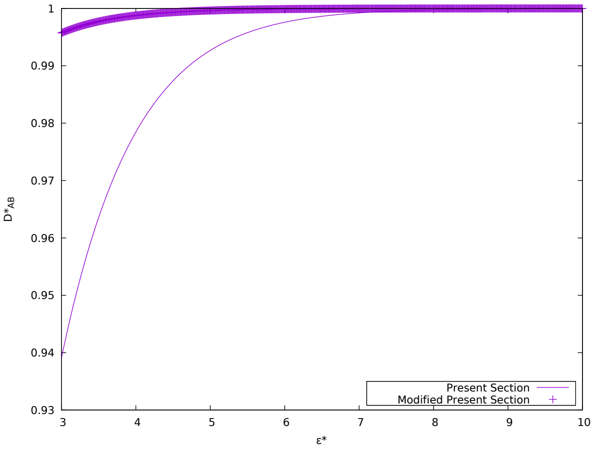

Figura 2: Dimensionless Diffusion Coefficient as a function of the activation energy $\varepsilon^\star$ with $x_A = 0.6$

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. Furthermore, the geometry of the collision was taken in to account by introducing a modification into the line-of-center differential cross section so that a chemical reaction takes place only when the energy of the relative velocity in the direction of the line which joins the centers of the molecules at collision is larger than the activation energy. The reaction heat modifies the diffusion coefficient and it shows that the reaction occurs only when the relative translational energy is greater than the activation energy. The effects on the diffusion coefficient is big for endothermic reactions than exothermic reactions.

6. ACKNOWLEDGMENTS

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