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# Analysis of the Reaction Rate Coefficients for Slow Bimolecular Chemical Reactions

Gilberto M. Kremer · Tiago G. Silva

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**Abstract** Simple bimolecular reactions  $A_1 + A_2 \rightleftharpoons A_3 + A_4$  are analyzed within the framework of the Boltzmann equation in the initial stage of a chemical reaction with the system far from chemical equilibrium. The Chapman–Enskog methodology is applied to determine the coefficients of the expansion of the distribution functions in terms of Sonine polynomials for peculiar molecular velocities. The results are applied to the reaction  $H_2 + Cl \rightleftharpoons HCl + H$ , and the influence of the non-Maxwellian distribution and of the activation-energy dependent reactive cross sections upon the forward and reverse reaction rate coefficients are discussed.

**Keywords** Boltzmann equation · Chemically reactive flows · Reaction rates

## 1 Introduction

Since the works of Prigogine and collaborators in the 1950's, the study of chemically reacting gases by means of the Boltzmann equation has constituted a topic of research [1, 2]. The first article in this series analyzed the chemical reaction  $A + A \rightarrow B + C$  under the as-

sumption that the constituents have only translational energy and the reagents are more concentrated than the products [1]. The Boltzmann equation was solved by the Chapman–Enskog method, the distribution function was expanded to second order in the Sonine polynomials, and the reaction rate was determined for two kinds of reactive differential cross sections: one of them a step function, the other taking the activation energy into account.

The second work analyzed the chemical reaction  $A_0 + B \rightleftharpoons A_1 + B$  and gave attention to the reaction heat [2]. The dependence of the reaction rate on the activation energy and on the reaction heat were determined.

It has long been known that the reaction rate depends on the choice of the molecular interactions, and this motivated Present to propose the following expression for the reactive cross section [3, 4]:

$$\sigma^* = \begin{cases} 0, & E \leq \epsilon^*, \\ \pi D^2 [1 - (\epsilon^*/E)], & E > \epsilon^*. \end{cases} \quad (1)$$

where the formation of the activation complex is possible only when the distance between the molecular centers is equal to the parameter  $D$ , related to the diameters of the molecules. This cross section, known as the *line-of-centers model*, allows a chemical reaction whenever the relative translational energy of the molecules  $E$  is larger than the activation energy  $\epsilon^*$ .

In 1960 Ross and Mazur [5] analyzed the bimolecular chemical reaction  $A + B \rightleftharpoons C + D$  and extracted general expressions for the forward and reverse reaction rates and the entropy production from the Boltzmann equation. The distribution function was not determined explicitly from the Boltzmann equation so that no exact

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Dedicated to Professor I-Shih Liu on the occasion of his 70th birthday.

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expressions for the reaction rates and entropy production were derived. The solution of the Boltzmann equation for the distribution function from the expansion of the distribution function in Sonine polynomials and computation of the forward and reverse reaction rate were presented later by Present [6] and by Shizgal and Karplus [7–10].

Many contributions to the analysis of chemically reactive systems follow these works. Among others we quote Refs. [11–32].

The cross sections determining the reactive collision term can be divided into two types, namely with and without activation energy [33, 34]. In general, cross sections with activation energy allow a reaction to occur whenever the relative translational energy exceeds the activation energy, as in (1). Even the slightest grazing collision leads to a chemical reaction. In a more realistic scenario, a reaction occurs only when the relative translational energy in the direction of the line joining the centers of the molecules is larger than the activation energy [11, 31, 34]. In this case the geometry of the collision plays a fundamental role in controlling the occurrence of a reaction.

Another important issue in applications of the Chapman–Enskog to the reactive Boltzmann equation is the distortion of the Maxwellian distribution functions by the reaction heat [2, 14, 26, 31], which makes the reaction rate coefficients sensitive to the reaction heat.

The aim of this work is to analyze the influence of the activation-energy cross sections and of the non-Maxwellian distribution function on the reaction-rate coefficients. Although relying on the same method adopted in the above-mentioned works, we here solve the Boltzmann equation for the distribution function, which we expand in Sonine polynomials up to second order. The reactive differential cross section we consider allows reactions only when the relative translational energy in the direction of the line joining the centers of the molecules is greater than the activation energy, and we analyze slow reactions. In other words, we analyze the initial stage of a chemical reaction, in which the system is far from chemical equilibrium. In this stage the elastic collisions are more frequent than reactive ones, and the affinity is much larger than the thermal energy of the mixture. We show that the reactive cross section under study markedly influences the reaction rates, while the effect of the non-Maxwellian distribution is not too pronounced.

The work is structured as follows: Section 2 introduces the system of Boltzmann equations for a sim-

ple bimolecular chemical reaction  $A_1 + A_2 \rightleftharpoons A_3 + A_4$ . The expressions for the reaction rate coefficients that follow from the Boltzmann equation and the specification of the elastic and reactive cross sections are the subject of Section 3. In Section 4 the Arrhenius equation is obtained from a Maxwellian distribution function. It is shown that the reaction-rate coefficient when the relative translational energy in the direction of the line which joins the centers of the molecules must be larger than the activation energy is different from the coefficient when only the relative translational energy must be greater than the activation energy. The analysis of the slow chemical reactions is the subject of Section 5, where the distribution functions are expanded in Sonine polynomials of the peculiar molecular velocity and the first coefficients of the expansions are obtained with the Chapman–Enskog methodology. In Section 6 the results of the previous section are applied to the chemical reaction  $H_2 + Cl \rightleftharpoons HCl + H$ , and the coefficients of the non-Maxwellian distribution function, and the forward and reverse reaction coefficients are plotted as functions of the temperature. The results show the effect of the non-Maxwellian distribution functions and of the reactive cross sections on the reaction-rate coefficients and on the entropy production rate.

## 2 Boltzmann Equations

We consider a simple reversible bimolecular gas reaction characterized by the chemical law  $A_1 + A_2 \rightleftharpoons A_3 + A_4$ , which takes elastic and reactive binary encounters between the molecules into account.

The elastic collisions between the two constituent molecules, of masses  $m_\alpha$  and  $m_\beta$ , have asymptotic pre-collisional velocities  $(\mathbf{c}_\alpha, \mathbf{c}_\beta)$ , asymptotic post-collisional velocities  $(\mathbf{c}'_\alpha, \mathbf{c}'_\beta)$ , and asymptotic relative velocities  $\mathbf{g}_{\beta\alpha} = \mathbf{c}_\beta - \mathbf{c}_\alpha$  and  $\mathbf{g}'_{\beta\alpha} = \mathbf{c}'_\beta - \mathbf{c}'_\alpha$ , respectively, so that the conservation laws of linear momentum and energy are given by the expressions

$$m_\alpha \mathbf{c}_\alpha + m_\beta \mathbf{c}_\beta = m_\alpha \mathbf{c}'_\alpha + m_\beta \mathbf{c}'_\beta, \quad (2)$$

$$\frac{1}{2} m_\alpha c_\alpha^2 + \frac{1}{2} m_\beta c_\beta^2 = \frac{1}{2} m_\alpha c_\alpha'^2 + \frac{1}{2} m_\beta c_\beta'^2, \quad (3)$$

respectively, where  $\alpha, \beta = 1, \dots, 4$ . The energy conservation law can also be written in terms of the asymptotic relative velocities as  $g_{\beta\alpha} = g'_{\beta\alpha}$ .

For a reactive collision the conservation laws of mass, linear momentum and total energy read

$$m_1 + m_2 = m_3 + m_4, \quad (4)$$

$$m_1 \mathbf{c}_1 + m_2 \mathbf{c}_2 = m_3 \mathbf{c}_3 + m_4 \mathbf{c}_4, \quad (5)$$

$$\epsilon_1 + \frac{1}{2} m_1 c_1^2 + \epsilon_2 + \frac{1}{2} m_2 c_2^2 = \epsilon_3 + \frac{1}{2} m_3 c_3^2 + \epsilon_4 + \frac{1}{2} m_4 c_4^2, \quad (6)$$

respectively. Here  $\epsilon_\alpha$  denotes the molecular binding energy ( $\alpha = 1, \dots, 4$ ), while  $(\mathbf{c}_1, \mathbf{c}_2)$  are the velocities of the reactants, and  $(\mathbf{c}_3, \mathbf{c}_4)$ , the velocities of the products of the forward reaction. The conservation law for the total energy (6) can be written in terms of the relative velocities  $g_{\beta\alpha} = |\mathbf{g}_{\beta\alpha}| = |\mathbf{c}_\beta - \mathbf{c}_\alpha|$  and of the heat of reaction  $Q$ —defined as the difference of the chemical binding energies of the products and the reactants  $Q = \epsilon_3 + \epsilon_4 - \epsilon_1 - \epsilon_2$ —as

$$\frac{1}{2} m_{12} g_{21}^2 = \frac{1}{2} m_{34} g_{43}^2 + Q, \quad (7)$$

where  $m_{\alpha\beta} = m_\alpha m_\beta / (m_\alpha + m_\beta)$  denotes the reduced mass.

We characterize the state of a reacting gaseous mixture in the phase space spanned by the positions  $\mathbf{x}$  and velocities  $\mathbf{c}_\alpha$  of the molecules by the set of distribution functions  $f_\alpha \equiv f(\mathbf{x}, \mathbf{c}_\alpha, t)$  with  $\alpha = 1, \dots, 4$ . The distribution function  $f_\alpha$  is defined so that the number of  $\alpha$  molecules in the volume element  $d\mathbf{x}d\mathbf{c}_\alpha$  around the position  $\mathbf{x}$  and the velocity  $\mathbf{c}_\alpha$  at time  $t$  is given by  $f_\alpha d\mathbf{x}d\mathbf{c}_\alpha$ .

The phase-space evolution of the distribution function  $f_\alpha$  for constituent  $\alpha$  is governed by the Boltzmann equation, which in the absence of external forces reads

$$\frac{\partial f_\alpha}{\partial t} + c_i^\alpha \frac{\partial f_\alpha}{\partial x_i} = \sum_{\beta=1}^4 \int (f'_\alpha f'_\beta - f_\alpha f_\beta) g_{\beta\alpha} \sigma_{\beta\alpha} d\Omega d\mathbf{c}_\beta + Q_\alpha^R, \quad \alpha = 1, \dots, 4, \quad (8)$$

with the shorthand  $f'_\alpha \equiv f_\alpha(\mathbf{x}, \mathbf{c}'_\alpha, t)$ .

The left-hand side of (8) refers to the space-time evolution of the distribution function, while its right-hand side takes the molecular collisions into account. The latter has two terms. The first one describes the elastic interactions among the constituents. In the integrand, the factor  $\sigma_{\alpha\beta}$  is the differential elastic cross section, and  $d\Omega = \sin \chi d\chi d\varepsilon$  the solid-angle element, with  $\chi$  denoting the scattering angle, and  $\varepsilon$ , the azimuthal angle that characterizes the collision.

The second term  $Q_\alpha^R$  on the right-hand side of (8) is related to the reactive collisions. The expression for the constituent labeled by the index 1 is obtained as follows. The number of reactive collisions for the forward reaction  $A_1 + A_2 \rightarrow A_3 + A_4$  per unit of volume and time is given by  $(f_1 f_2 g_{21} \sigma_{12}^* d\Omega^* d\mathbf{c}_1 d\mathbf{c}_2)$ , where  $\sigma_{12}^*$  represents the reactive differential cross section and  $d\Omega^*$  is the solid-angle element relating the orientation of the post-collisional relative velocity  $\mathbf{g}_{43}$  with respect to the pre-collisional one  $\mathbf{g}_{21}$ . Likewise, the number of collisions for the reverse reaction  $A_1 + A_2 \leftarrow A_3 + A_4$  reads  $(f_3 f_4 g_{43} \sigma_{34}^* d\Omega^* d\mathbf{c}_3 d\mathbf{c}_4)$ . For a fixed value of the heat of reaction it follows from (7) that  $m_{12} g_{21} dg_{21} = m_{34} g_{43} dg_{43}$ , and we also may obtain the equality  $m_{34} g_{21} d\mathbf{c}_3 d\mathbf{c}_4 = m_{12} g_{43} d\mathbf{c}_1 d\mathbf{c}_2$ . Furthermore, for small heats of reaction the principle of microscopic reversibility yields  $(m_{12} g_{21})^2 \sigma_{12}^* = (m_{34} g_{43})^2 \sigma_{34}^*$ . Hence, all relationships accounted for, we find that  $f_3 f_4 g_{43} \sigma_{34}^* d\Omega^* d\mathbf{c}_3 d\mathbf{c}_4 = f_1 f_2 (m_{12}/m_{34})^3 g_{21} \sigma_{12}^* d\Omega^* d\mathbf{c}_1 d\mathbf{c}_2$ . From the difference of the expressions for the number of collisions in the backward and forward reactions divided by  $d\mathbf{c}_1$  and integrated over all values of  $d\mathbf{c}_2$  and  $d\Omega^*$ , we obtain the following expression for the reactive collision term for the constituent labeled 1:

$$Q_{1(2)}^R = \int \left[ f_3 f_4 \left( \frac{m_{12}}{m_{34}} \right)^3 - f_1 f_2 \right] \sigma_{12}^* g_{21} d\Omega^* d\mathbf{c}_{2(1)}. \quad (9)$$

The reactive collision term for the constituent labeled by the index 2 being similar, the terms within parentheses in (9) determine  $Q_2^R$ . In the same notation, the reactive collision terms for the constituents labeled by the indexes 3 and 4 read

$$Q_{3(4)}^R = \int \left[ f_1 f_2 \left( \frac{m_{34}}{m_{12}} \right)^3 - f_3 f_4 \right] \sigma_{34}^* g_{43} d\Omega^* d\mathbf{c}_{4(3)}. \quad (10)$$

### 3 Reaction Rates and Differential Cross Sections

The description of the evolution equation for the particle number density  $n_\alpha = \int f_\alpha d\mathbf{c}_\alpha$  of constituent  $\alpha$  is obtained by integrating the Boltzmann equation (8) over all values of  $\mathbf{c}_\alpha$ , which yields

$$\frac{\partial n_\alpha}{\partial t} + \frac{\partial n_\alpha v_i^\alpha}{\partial x_i} = \tau_\alpha. \quad (11)$$

Here, the bulk velocity  $v_i^\alpha$  and the particle number density production  $\tau_\alpha$  of the constituent  $\alpha$  read

$$v_i^\alpha = \frac{1}{n_\alpha} \int c_i^\alpha f_\alpha d\mathbf{c}_\alpha, \quad \tau_\alpha = -v_\alpha (n_3 n_4 k_r - n_1 n_2 k_f), \quad (12)$$

where  $k_f$  and  $k_r$  denote the forward and reverse reaction rate coefficients, respectively. They are defined by

$$k_f = \frac{1}{n_1 n_2} \int f_1 f_2 \sigma_{12}^* g_{21} d\Omega^* d\mathbf{c}_1 d\mathbf{c}_2, \quad k_r = \frac{1}{n_3 n_4} \int f_3 f_4 \left( \frac{m_{12}}{m_{34}} \right)^3 \sigma_{12}^* g_{21} d\Omega^* d\mathbf{c}_1 d\mathbf{c}_2. \quad (13)$$

In (12)<sub>2</sub> we have introduced the stoichiometric coefficients  $\nu_\alpha$  of the constituent  $\alpha$ , which for the chemical reaction  $A_1 + A_2 \rightleftharpoons A_3 + A_4$  are given by  $\nu_1 = \nu_2 = -\nu_3 = -\nu_4 = -1$ .

In order to determine the distribution functions  $f_\alpha$  from the system of Boltzmann equations (8), we have to specify the elastic and the reactive differential cross sections. We assume that the elastic differential cross sections correspond to a hard-sphere potential, i.e., that

$$\sigma_{\alpha\beta} = \frac{1}{4} d_{\alpha\beta}^2, \quad d_{\alpha\beta} = \frac{1}{2} (d_\alpha + d_\beta), \quad (14)$$

where  $d_\alpha$  and  $d_\beta$  represent the diameters of the colliding spheres.

For the reactive differential cross section we shall use the modified line-of-centers model [11, 31, 34]

$$\sigma_{12}^* = \begin{cases} 0, & m_{12} (\mathbf{k}_{21} \cdot \mathbf{g}_{21})^2 / 2 < \epsilon_f, \\ \frac{1}{4} \mathbf{s}_f d_{12}^2 \left[ 1 - \frac{2\epsilon_f}{m_{12} (\mathbf{k}_{21} \cdot \mathbf{g}_{21})^2} \right], & m_{12} (\mathbf{k}_{21} \cdot \mathbf{g}_{21})^2 / 2 \geq \epsilon_f, \end{cases} \quad (15a)$$

$$\sigma_{34}^* = \begin{cases} 0, & m_{34} (\mathbf{k}_{43} \cdot \mathbf{g}_{43})^2 / 2 < \epsilon_r, \\ \frac{1}{4} \mathbf{s}_r d_{34}^2 \left[ 1 - \frac{2\epsilon_r}{m_{34} (\mathbf{k}_{43} \cdot \mathbf{g}_{43})^2} \right], & m_{34} (\mathbf{k}_{43} \cdot \mathbf{g}_{43})^2 / 2 \geq \epsilon_r. \end{cases} \quad (15b)$$

Here  $\epsilon_f$  and  $\epsilon_r$  denote the forward and reverse activation energies, respectively, and  $\mathbf{s}_f$  and  $\mathbf{s}_r$  the corresponding steric factors, while  $\mathbf{k}_{21}$  and  $\mathbf{k}_{43}$  are unit collision vectors in the directions of the centers of the colliding molecules pointing from the centers of 2 and 4 to the centers of 1 and 3, respectively.

The differential cross sections in (15a) and (15b) take into account the activation energies and the geometry of the reactive collisions, since they are functions of the relative translational energies in the direction of the lines joining the centers of the molecules  $m_{12} (\mathbf{k}_{21} \cdot \mathbf{g}_{21})^2$  and  $m_{34} (\mathbf{k}_{43} \cdot \mathbf{g}_{43})^2$ . The original line-of-centers model considers the relative translational energies as  $m_{12} g_{21}^2$  and  $m_{34} g_{43}^2$ , so that even the slightest grazing collision leads to a chemical reaction.

#### 4 Arrhenius Equation

For mixtures the chemical potential of the constituent  $\alpha$ , which takes into account the binding energy of the molecules—but not the internal states of the molecules

associated with the rotational, vibrational, electronic and nuclei states—is given by the equality

$$\mu_\alpha = \frac{kT}{m_\alpha} \left[ \frac{\epsilon_\alpha}{kT} + \ln n_\alpha - \frac{3}{2} \ln T + C_\alpha \right], \quad (16)$$

where  $k$  denotes Boltzmann's constant,  $C_\alpha$  is a constant, and all constituents have been assumed to be at the temperature  $T$  of the mixture, defined by

$$T = \frac{1}{3kn_\alpha} \int m_\alpha |\mathbf{c}_\alpha - \mathbf{v}_\alpha|^2 f_\alpha d\mathbf{c}_\alpha. \quad (17)$$

Chemical equilibrium is characterized by the condition

$$\sum_{\alpha=1}^4 m_\alpha \nu_\alpha \mu_\alpha^{\text{eq}} = 0, \quad (18)$$

where the index “eq” denotes the equilibrium-value of the chemical potential. Out-of-equilibrium chemical reactions are described by the affinity, defined as

$$\mathcal{A} = - \sum_{\alpha=1}^4 m_\alpha \nu_\alpha \mu_\alpha, \quad \text{with} \quad \mathcal{A}^{\text{eq}} = 0. \quad (19)$$

From the above equations we can obtain the law of mass action,

$$\ln \left[ \frac{n_1^{\text{eq}} n_2^{\text{eq}}}{n_3^{\text{eq}} n_4^{\text{eq}}} \left( \frac{m_3 m_4}{m_1 m_2} \right)^{\frac{3}{2}} \right] = Q^*, \quad (20)$$

and the following expression for the affinity

$$\ln \left[ \frac{n_1 n_2 n_3^{\text{eq}} n_4^{\text{eq}}}{n_3 n_4 n_1^{\text{eq}} n_2^{\text{eq}}} \right] = \mathcal{A}^*, \quad (21)$$

where we have introduced the dimensionless reaction heat  $Q^* = Q/kT$  and affinity  $\mathcal{A}^* = \mathcal{A}/kT$ , in units of the thermal energy  $kT$ .

The state of equilibrium of a non-reacting gas mixture is characterized by the Maxwellian distribution functions

$$f_\alpha^{(0)} = n_\alpha \left( \frac{m_\alpha}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{m_\alpha \xi_\alpha^2}{2kT}}, \quad \alpha = 1, \dots, 4, \quad (22)$$

where the particle number densities are uncorrelated.

In fact, these distribution functions make the elastic collision terms of the Boltzmann equation (8) equal to zero. In general, however, the reactive collision terms (9) and (10) do not vanish, because the particle number densities in the distribution functions (22) are not the equilibrium densities, which characterize the chemical equilibrium and are related by the law of mass action, Eq. (20). In (22) we have introduced the peculiar velocity  $\xi_i^\alpha = c_i^\alpha - v_i$  where  $v_i = \sum_{\alpha=1}^4 \varrho_\alpha v_i^\alpha / \sum_{\alpha=1}^4 \varrho_\alpha$  is the bulk velocity of the mixture.

From the Maxwellian distribution functions we can calculate the forward reaction rate coefficient by substituting (22) in the definition of the forward reaction rate coefficient, (13). Substitution of the differential cross section (15a) and integration of the resulting equation leads to the result

$$\begin{aligned} k_f^{(0)} &= \frac{(m_1 m_2)^{\frac{3}{2}}}{(2\pi kT)^3} \int \exp \left[ -\frac{(m_1 + m_2)G_{12}^2}{2kT} - \frac{m_{12}g_{21}^2}{2kT} \right] \\ &\quad \times \mathbf{s}_f d_{12}^2 \left[ 1 - \frac{2\epsilon_f}{m_{12}(g_{21} \cos \theta)^2} \right] \\ &\quad \times g_{21} \sin \theta \cos \theta d\theta d\epsilon d\mathbf{g}_{21} d\mathbf{G}_{12}, \end{aligned} \quad (23)$$

since the solid-angle element is  $d\Omega^* = 4 \sin \theta \cos \theta d\theta d\epsilon$  where  $\theta$  and  $\epsilon$  are the angles characterizing the reactive collision process, while  $\mathbf{k}_{21} \cdot \mathbf{g}_{21} = g_{21} \cos \theta$ . We have introduced the relative velocity  $\mathbf{g}_{21}$  and the center of mass velocity  $\mathbf{G}_{12}$  defined by the relation

$$g_i^{\alpha\beta} = \xi_i^\beta - \xi_i^\alpha, \quad G_i^{\alpha\beta} = \frac{m_\alpha \xi_i^\alpha + m_\beta \xi_i^\beta}{m_\alpha + m_\beta}. \quad (24)$$

The range of the integrals in the variables  $G_{12}$  and  $\epsilon$  on the right-hand side of (23) are  $0 \leq G_{12} < \infty$  and  $0 \leq \epsilon \leq 2\pi$ , respectively. The range of the integral over the angle  $\theta$  follows from (15a), according to which the normal relative velocity has a lower bound so that the interval of integration of  $\theta$  is given by  $0 \leq \theta \leq \arccos \sqrt{2\epsilon_f/m_{12}g_{21}^2}$ . The range of the relative velocity is  $\sqrt{2\epsilon_f/m_{12}} \leq g_{12} < \infty$ .

From the integration of (23) we obtain the following expression for the forward reaction rate coefficient

$$k_f^{(0)} = \sqrt{\frac{8\pi kT}{m_{12}}} \mathbf{s}_f^2 d_{12}^2 e^{-\epsilon_f^*} \left( 1 - \epsilon_f^* E_1(\epsilon_f^*) e^{\epsilon_f^*} \right), \quad (25)$$

a modified Arrhenius equation. Here,  $\epsilon_f^*$  is the forward activation energy in units of the thermal energy  $kT$ , and  $E_1(\epsilon_f^*)$  represents the exponential integral  $E_1(\epsilon_f^*) = \int_{\epsilon_f^*}^{\infty} \frac{e^{-y} dy}{y}$ .

The underlined term in (25) is the usual Arrhenius equation, which follows from substituting  $m_{12}g_{21}^2$  for  $m_{12}(\mathbf{k}_{21} \cdot \mathbf{g}_{21})^2$  in the differential cross section. Inspection of (25) shows that the reaction-rate coefficient is smaller for the latter case, in which a reaction occurs only when the relative translational energy in the direction of the line which joins the molecular centers exceeds the activation energy. In the former case even a grazing collision with relative translational energy larger than the activation energy would lead to a chemical reaction.

## 5 Slow Chemical Reactions

When dealing with chemical reactions within the framework of the Boltzmann equation, we can analyze two regimes:

**Fast reactions:** the last stage of a chemical reaction. The system is nearby a chemical equilibrium state. The frequencies of the elastic and reacting collisions are of the same order of magnitude and the affinity is small in comparison with the thermal energy of the mixture, i.e.,  $\mathcal{A} \ll kT$ ;

**Slow reactions:** the initial stage of a chemical reaction. The system is far from chemical equilibrium. The elastic collisions are much more frequent than the reactive ones and the affinity is much larger than the thermal energy of the mixture, i.e.,  $\mathcal{A} \gg kT$ .

In this work we shall analyze slow reactions. We write the Boltzmann equations in the form

$$\begin{aligned} \mathcal{D} f_{\alpha} + \lambda \xi_i^{\alpha} \frac{\partial f_{\alpha}}{\partial x_i} - \int \left[ f_3 f_4 \left( \frac{m_{12}}{m_{34}} \right)^3 - f_1 f_2 \right] \sigma_{12}^* g_{21} d\Omega^* d\mathbf{c}_{\gamma} \\ = \frac{1}{\lambda} \sum_{\beta=1}^4 \int (f'_{\alpha} f'_{\beta} - f_{\alpha} f_{\beta}) g_{\beta\alpha} \sigma_{\beta\alpha} d\Omega d\mathbf{c}_{\beta}, \end{aligned} \quad (26a)$$

$$\begin{aligned} \mathcal{D} f_{\alpha} + \lambda \xi_i^{\alpha} \frac{\partial f_{\alpha}}{\partial x_i} - \int \left[ f_1 f_2 \left( \frac{m_{34}}{m_{12}} \right)^3 - f_3 f_4 \right] \sigma_{34}^* g_{43} d\Omega^* d\mathbf{c}_{\gamma} \\ = \frac{1}{\lambda} \sum_{\beta=1}^4 \int (f'_{\alpha} f'_{\beta} - f_{\alpha} f_{\beta}) g_{\beta\alpha} \sigma_{\beta\alpha} d\Omega d\mathbf{c}_{\beta}, \end{aligned} \quad (26b)$$

where  $\mathcal{D} = \partial/\partial t + v_i \partial/\partial x_i$  is the material time derivative, and  $\lambda$  a parameter of the order of the Knudsen number. In (26a)  $\alpha = 1, 2$  corresponds to  $\gamma = 2, 1$ , while in (26b)  $\alpha = 3, 4$ , to  $\gamma = 4, 3$ . Since we assumed the elastic collisions to be more frequent than the reactive ones, (26a) and (26b) indicate that the reactive collision terms and the material time derivatives are of the same order of magnitude, while the gradients of the particle number densities, velocity and temperature of the mixture are of the next order.

To obtain the distribution functions from (26a) and (26b) we apply the Chapman–Enskog methodology. To that end, we expand the material time derivative in a power series of a parameter  $\lambda$ , i. e., we write

$$\mathcal{D} = \mathcal{D}_0 + \lambda \mathcal{D}_1 + \lambda^2 \mathcal{D}_2 + \dots, \quad (27)$$

along with the distribution functions

$$f_{\alpha} = f_{\alpha}^{(0)} + \lambda f_{\alpha}^{(1)} + \lambda^2 f_{\alpha}^{(2)} + \dots, \quad \alpha = 1, \dots, 4. \quad (28)$$

The parameter  $\lambda$  in the distribution function will be set equal to the unit later.

We insert the expansions (27) and (28) into the Boltzmann equations (26a) and (26b). Comparison of equal powers of  $\lambda$  leads to the following system of integral equations:

$$0 = \sum_{\beta=1}^4 \int (f_{\alpha}^{(0)'} f_{\beta}^{(0)'} - f_{\alpha}^{(0)} f_{\beta}^{(0)}) g_{\beta\alpha} \sigma_{\beta\alpha} d\Omega d\mathbf{c}_{\beta}, \quad (29)$$

$$\begin{aligned} \mathcal{D}_0 f_{\alpha}^{(0)} - \int \left[ f_3^{(0)} f_4^{(0)} \left( \frac{m_{12}}{m_{34}} \right)^3 - f_1^{(0)} f_2^{(0)} \right] \sigma_{12}^* g_{21} d\Omega^* d\mathbf{c}_{\gamma} \\ = \sum_{\beta=1}^4 \int [f_{\alpha}^{(1)'} f_{\beta}^{(0)'} + f_{\alpha}^{(0)'} f_{\beta}^{(1)'} - f_{\alpha}^{(1)} f_{\beta}^{(0)} - f_{\alpha}^{(0)} f_{\beta}^{(1)}] \\ \times g_{\beta\alpha} \sigma_{\beta\alpha} d\Omega d\mathbf{c}_{\beta}, \quad \alpha = 1, 2 \quad \gamma = 2, 1, \end{aligned} \quad (30)$$

$$\begin{aligned} \mathcal{D}_0 f_{\alpha}^{(0)} - \int \left[ f_1^{(0)} f_2^{(0)} \left( \frac{m_{34}}{m_{12}} \right)^3 - f_3^{(0)} f_4^{(0)} \right] \sigma_{34}^* g_{43} d\Omega^* d\mathbf{c}_{\gamma} \\ = \sum_{\beta=1}^4 \int [f_{\alpha}^{(1)'} f_{\beta}^{(0)'} + f_{\alpha}^{(0)'} f_{\beta}^{(1)'} - f_{\alpha}^{(1)} f_{\beta}^{(0)} - f_{\alpha}^{(0)} f_{\beta}^{(1)}] \\ \times g_{\beta\alpha} \sigma_{\beta\alpha} d\Omega d\mathbf{c}_{\beta}, \quad \alpha = 3, 4 \quad \gamma = 4, 3. \end{aligned} \quad (31)$$

Here we have only considered the integral equations to first order in  $\lambda$ , i. e., associated with the zeroth order term  $f_{\alpha}^{(0)}$  and the first-order correction  $f_{\alpha}^{(1)}$ .

The solution of the integral equation (29) is the Maxwellian distribution function (22). To solve the integral equations (30) and (31) we assume that the reaction heat affects the Maxwellian distribution functions, so that  $f_{\alpha}^{(1)}$  can be expressed in terms of Sonine polynomials in the peculiar velocity  $\xi_i^{\alpha}$ , i.e.,

$$f_{\alpha}^{(1)} = f_{\alpha}^{(0)} \sum_{n=1}^{\infty} a_{n\alpha} S_{\frac{1}{2}}^{(n)} \left( \frac{m_{\alpha} \xi_{\alpha}^2}{2kT} \right), \quad \text{where}$$

$$S_{\frac{1}{2}}^{(n)}(x) = \sum_{k=0}^n \frac{\Gamma(n+3/2)}{k!(n-k)!\Gamma(k+3/2)} (-x)^k. \quad (32)$$

The coefficients  $a_{n\alpha}$  are constants to be determined from the integral equations. Up to second order terms in the expansion, the distribution function can be written as

$$\begin{aligned} f_{\alpha} = f_{\alpha}^{(0)} \left[ 1 + a_{1\alpha} \left( \frac{3}{2} - \frac{m_{\alpha} \xi_{\alpha}^2}{2kT} \right) \right. \\ \left. + a_{2\alpha} \left( \frac{15}{8} - \frac{5m_{\alpha} \xi_{\alpha}^2}{4kT} + \frac{m_{\alpha}^2 \xi_{\alpha}^4}{8(kT)^2} \right) \right], \\ \alpha = 1, \dots, 4. \end{aligned} \quad (33)$$

Insertion of the distribution function (33) into the definition (17) of the temperature of constituent  $\alpha$ , shows that all coefficients  $a_{1\alpha}$  are zero. To determine the remaining coefficients  $a_{2\alpha}$  we multiply (30) and

(31) by the Sonine polynomial  $[15/8 - 5m_\alpha \xi_\alpha^2/4kT + m_\alpha^2 \xi_\alpha^4/8(kT)^2]$  and integrate over all  $d\mathbf{c}_\alpha$ , which shows that

$$- \frac{(1 - e^{-A^*}) s_f^2 d_{12}^2 e^{-\epsilon_f^*} \left[ 1 - 4\epsilon_f^* + 3\epsilon_f^* E_1(\epsilon_f^*) e^{\epsilon_f^*} \right] m_{12}^{\frac{3}{2}} n_1 n_2}{8m_\alpha^2} \\ = \sum_{\beta=1}^4 \frac{n_\alpha n_\beta \sqrt{m_{\alpha\beta}}}{(m_\alpha + m_\beta)^2} d_{\alpha\beta}^2 \left\{ \frac{10m_\alpha^2 + 8m_\alpha m_\beta + 13m_\beta^2}{m_\alpha + m_\beta} a_{2\alpha} - 15m_{\alpha\beta} a_{2\beta} \right\}, \quad \alpha = 1, 2; \quad (34)$$

$$\frac{(1 - e^{-A^*}) s_f^2 d_{12}^2 e^{-\epsilon_f^*} \left\{ 1 - 4\epsilon_f^* + 3\epsilon_f^* E_1(\epsilon_f^*) e^{\epsilon_f^*} - 4Q^* \left[ 1 + Q^* - \epsilon_f^* E_1(\epsilon_f^*) e^{\epsilon_f^*} (3 + Q^*) \right] \right\} m_{34}^5 n_1 n_2}{8m_\alpha^2 m_{12}^{\frac{7}{2}}} \\ = \sum_{\beta=1}^4 \frac{n_\alpha n_\beta \sqrt{m_{\alpha\beta}}}{(m_\alpha + m_\beta)^2} d_{\alpha\beta}^2 \left\{ \frac{10m_\alpha^2 + 8m_\alpha m_\beta + 13m_\beta^2}{m_\alpha + m_\beta} a_{2\alpha} - 15m_{\alpha\beta} a_{2\beta} \right\}, \quad \alpha = 3, 4. \quad (35)$$

From the algebraic system of (34) and (35) we can determine the four coefficients  $a_{21}, \dots, a_{24}$  of the distribution functions (33). The expressions for these coefficients are too long to be presented here.

To determine the forward and reverse reaction rate coefficients, we insert each distribution function (32) in

the corresponding definition, in (13). Integration of the resulting equalities then yields the expressions

$$k_f = k_f^{(0)} \left\{ 1 - \frac{1 - 4\epsilon_f^* + 3\epsilon_f^* E_1(\epsilon_f^*) e^{\epsilon_f^*}}{1 - \epsilon_f^* E_1(\epsilon_f^*) e^{\epsilon_f^*}} \frac{a_{21} m_2^2 + a_{22} m_1^2}{8(m_1 + m_2)^2} \right\}, \quad (36)$$

$$k_r = \left( \frac{m_1 m_2}{m_3 m_4} \right)^{\frac{3}{2}} e^{Q^*} k_f^{(0)} \left\{ 1 - \frac{1 - 4(\epsilon_f^* + Q^* + Q^{*2}) + \epsilon_f^* E_1(\epsilon_f^*) e^{\epsilon_f^*} (3 + 12Q^* + 4Q^{*2})}{1 - \epsilon_f^* E_1(\epsilon_f^*) e^{\epsilon_f^*}} \frac{a_{23} m_4^2 + a_{24} m_3^2}{8(m_3 + m_4)^2} \right\}. \quad (37)$$

The underlined terms are corrections to the forward and reverse reaction rate coefficients, for non-Maxwellian distribution functions. The corrections depend on the coefficients  $a_{21}, \dots, a_{24}$  of the distribution functions (33), on the reaction heat, and on the activation energy of the forward reaction.

the molecular weights  $M_\alpha$  and the coefficients of shear viscosity  $\mu_\alpha$  at temperature  $T = 293$  K for the single constituents  $H$ ,  $H_2$ ,  $Cl$  and  $HCl$  [35]. From the expression of the coefficient of shear viscosity for hard-sphere molecules (see e.g. [34])

$$\mu_\alpha = \frac{5}{16d_\alpha^2} \sqrt{\frac{m_\alpha kT}{\pi}}, \quad (38)$$

## 6 Reaction rates for $H_2 + Cl \rightleftharpoons HCl + H$

We now apply the results of Sections 4 and 5 to evaluate the rate coefficients for the reaction  $H_2 + Cl \rightleftharpoons HCl + H$ . To that end we need to know certain characteristic parameters for the constituents of the mixture, such as masses, diameters, forward and reverse activation energies, reaction heat and steric factors. Table 1 lists

**Table 1** Molecular weights, viscosities and molecular diameters

Gas	H	H <sub>2</sub>	Cl	HCl
$M_\alpha$	1.008	2.016	35.453	36.461
$\mu_\alpha$ ( $\times 10^{-5}$ Pa s)	–	0.841	–	1.332
$d_\alpha$ ( $\times 10^{-10}$ m)	1.06	2.78	1.99	4.55

**Table 2** Arrhenius coefficients, forward and reverse activation energies, reaction heat and steric factors

Reaction	$A$ (m <sup>3</sup> /mol s)	$\epsilon_f$ (kJ/mol)	$\epsilon_r$ (kJ/mol)	$Q$ (kJ/mol)	$s_f$
$H_2 + Cl \rightarrow HCl + H$	$7.94 \times 10^7$	23.03	18.84	4.19	0.648
$HCl + H \rightarrow H_2 + Cl$	$4.68 \times 10^7$	18.84	23.03	-4.19	0.497

we can calculate the diameters of the single constituents  $H_2$  and  $HCl$ . For the constituent  $Cl$  we take the diameter to be twice the atomic radius, whereas for the constituent  $H$  we take the diameter to be of order of twice the Bohr radius  $a_0 = 0.529 \times 10^{-10}$  m.

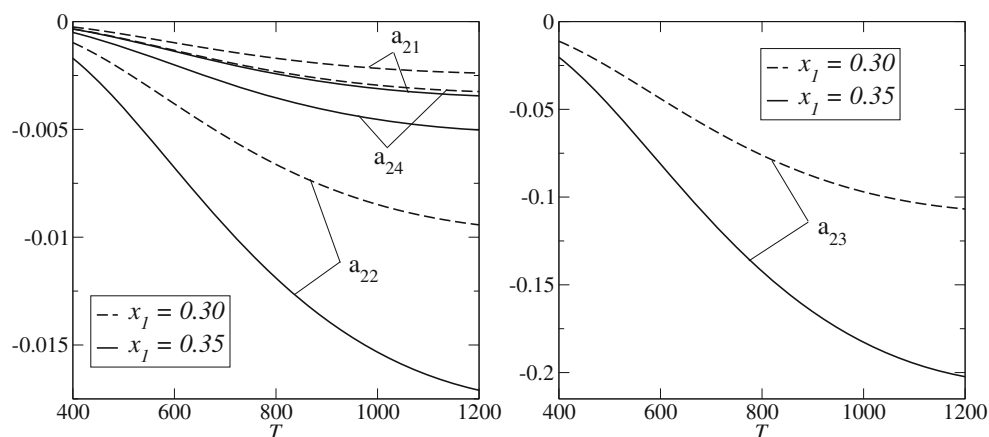
Table 2 lists the coefficient  $A$  of the Arrhenius equation  $k_f^{(0)} = Ae^{-\epsilon_f}$ , the forward, and the reverse activation energies [36]. The reference temperature for this reaction is 300 K and the reaction heat was obtained from the relation  $Q = \epsilon_f - \epsilon_r$ . The steric factors in this table were calculated from the identification  $A = \sqrt{8\pi kT/m_{12}} s_f^2 d_{12}^2$ , from (25).

To analyze a slow reaction, in which the concentrations of the reagents is larger than those of the products, we start out with a preliminary evaluation of the factor  $\left(\frac{m_1 m_2}{m_3 m_4}\right)^{\frac{3}{2}} e^{Q^*}$  appearing in the reverse reaction rate coefficient (37). If we adopt the tabulated values and consider the reaction in the direction  $H_2 + Cl \rightarrow HCl + H$ , a very large ratio results between the reverse and the forward reaction coefficients. We therefore discard this alternative and consider only the reaction in the direction  $HCl + H \rightarrow H_2 + Cl$ , for which the ratio is small.

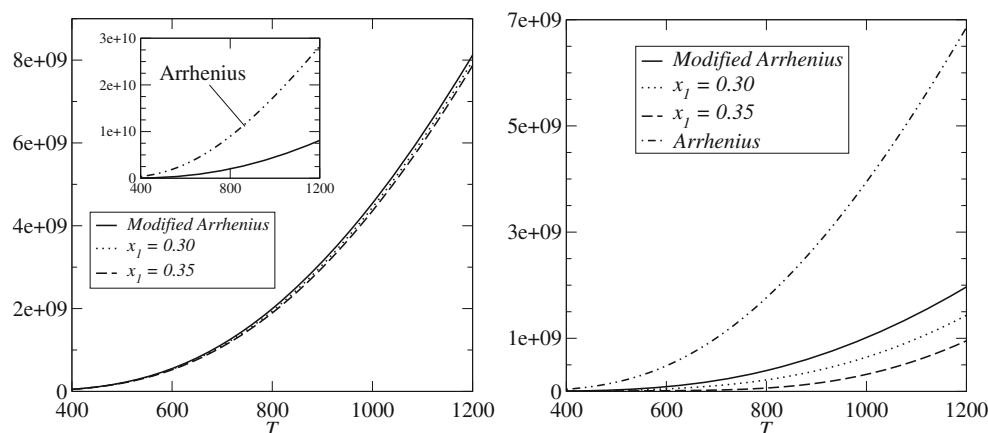
To determine the coefficients  $a_{2\alpha}$  from the algebraic system of (34) and (35) we need to know the temperature and the concentrations of the constituents  $x_\alpha = n_\alpha/n$  where  $n = \sum_{\beta=1}^4 n_\beta$  and  $\sum_{\alpha=1}^4 x_\alpha = 1$ . Here we analyze the case  $x_1 = x_2$  and  $x_3 = x_4$ . Figure 1 shows the coefficients  $a_{2\alpha}$ , plotted as functions of the temperature in the range  $400 \text{ K} \leq T \leq 1200 \text{ K}$  for two concentrations:  $x_1 = 0.30$  and  $x_1 = 0.35$ . The figure shows

that the deviations from the Maxwellian distribution functions—which are given by the coefficients  $a_{2\alpha}$ —increase with the temperature. In comparison with the departure for the constituent  $H_2$ , the departures for the constituents  $HCl$ ,  $H$  and  $Cl$  are not very large.

Figure 2 shows the dependence of the reaction rate coefficients on the temperature in the range  $400 \text{ K} \leq T \leq 1200 \text{ K}$ , for two concentrations:  $x_1 = 0.30$  and  $x_1 = 0.35$ . The left (right) panel represents the forward reaction (reverse reaction) rate coefficient. Consider first the influence of the collision geometry on the reaction rate coefficients. The dashed-dotted lines in the inset left panel and in the right panel represent the Arrhenius law, given by the underlined term in (25), while the solid lines correspond to the modified Arrhenius equation (25), when the geometry of the collision is taken into account, i.e., when a reaction occurs only if the relative translational energy in the direction of the line joining the molecular centers exceeds the activation energy. The reaction rates in the former case are larger than those in the latter, an indication that more reactions occur in the former case, due to the fact that even grazing collisions with translational energy larger than the activation energy lead to chemical reactions. In the same figures we also plot the influence of the departures from the Maxwellian distribution functions on the reaction rate coefficients. The left and the right panels show that the non-Maxwellian distribution functions reduce the reaction rate coefficients and that the forward reaction rate coefficient is less reduced than the reverse reaction one. The reduction becomes more pronounced as the reagent concentration grows.

**Fig. 1** Coefficients  $a_{2\alpha}$  as functions of the temperature for two concentrations: 0.30 and 0.35

**Fig. 2** Reaction rate coefficients in  $\text{dm}^3/(\text{mol s})$  as functions of temperature in K. *Left panel*: forward reaction rate; *right panel*: reverse reaction rate



Once the forward and reverse reaction rates are known, we can compute the entropy production rate. According to a phenomenological theory (see e.g. [37, 38]) the entropy-density rate  $\zeta$  is given by

$$\zeta = \frac{\mathcal{A}}{T} \frac{d\xi}{dt}, \quad \text{where} \quad \frac{d\xi}{dt} = k_f n_1 n_2 - k_r n_3 n_4, \quad (39)$$

the so-called reaction velocity.

Equation (39) can also be deduced from the Boltzmann equation; for more details see Ref. [5, 34]. In view of the law of mass action  $k_f n_1^{\text{eq}} n_2^{\text{eq}} = k_r n_3^{\text{eq}} n_4^{\text{eq}}$ , which shows that, in equilibrium, the forward and the reverse reactions occur with the same probability, the affinity (21) becomes

$$\mathcal{A} = kT \ln \left( \frac{k_f n_1 n_2}{k_r n_3 n_4} \right), \quad (40)$$

so that the entropy production rate (39) can be written as

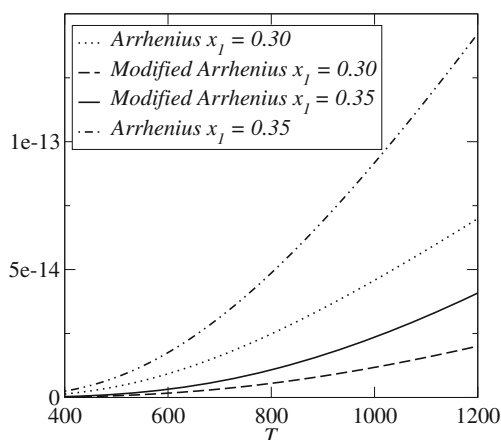
$$\frac{\zeta}{n^2} = k \ln \left( \frac{k_f x_1 x_2}{k_r x_3 x_4} \right) (k_f x_1 x_2 - k_r x_3 x_4). \quad (41)$$

As one would expect, the entropy production rate is positive semi-definite—thanks to the inequality  $(x - 1) \ln x \geq 0$  which is valid for all  $x > 0$ , the equality being valid for  $x = 1$ .

Figure 3 shows the entropy production rate (41) as a function of the temperature for the Arrhenius and modified Arrhenius cases, to show that in the former case the rate is larger than in the latter. This is expected, given the entropy production rate dependence on the reaction rates. For larger concentrations  $x_1$  the entropy production rate increases in both cases.

## 7 Conclusions

We have used the Boltzmann equation to analyze a bimolecular chemical reaction in its initial stage. As an illustration, we computed the reaction rates and the entropy production rate for the typical bimolecular reaction  $H_2 + Cl \rightleftharpoons HCl + H$ . To solve the Boltzmann equation by the Chapman–Enskog method we have expanded the distribution function in Sonine polynomials up to the second order. Our reactive differential cross section allows a reaction to occur only when the relative translational energy in the direction of the line of centers which joins the centers of the molecules is greater than the activation energy. With this cross section the calculated reaction rates are substantially smaller than those obtained from the line-of-centers model, which requires the relative translational energy to be larger than the activation energy. We showed that the restriction to large relative translational energies along the



**Fig. 3** Entropy production rate in  $\text{J dm}^3/(\text{K mol s})$  as function of the temperature in K

line of centers affects the calculated rates more than the departure from the Maxwellian distribution function.

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