The effect of heat conduction on the rate of chemical reaction in dilute gases

J. Fort a,*, A.S. Cukrowski b,c

a Secció de Física, Departament d’Enginyeria Industrial, Escola Politècnica Superior, Universitat de Girona, Avinguda Lluís Santaló s/n, 17071 Girona, Catalonia, Spain
b Institute of Physical Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44 / 52, 01-224 Warsaw, Poland
c Pedagogical University, Faculty of Mathematical and Natural Sciences, Institute of Chemistry, ul. Checinska 5, 25-020 Kielce, Poland

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Abstract

Information statistical theory is used to obtain the second-order terms (similar to those analyzed in the Burnett approximation to the solution of the Boltzmann equation) in the expansion of the nonequilibrium velocity distribution function. These terms are used for the evaluation of the effect of the heat flux on the rate of bimolecular chemical reactions. This effect is shown to be important for reactions characterized by high values of the activation energy. However, very large values of the heat flux would be necessary. The results are compared with those obtained earlier from the square terms calculated from the linearized Boltzmann equation and with recent results due to Nettleton. © 1997 Published by Elsevier Science B.V.

1. Introduction

As discussed by Prigogine and Xhouet [1], in the early stages of a bimolecular chemical reaction:

\[ A + A \rightarrow B + B \] (1)

both the concentration of products and the reverse reaction can be neglected. Therefore, for the early stages of the reaction (1), the chemical reaction:

\[ A + A \rightarrow B + B \] (2)

can be analyzed. Prigogine and Xhouet [1] were the first to show that it is enough to take into account Eq. (2) in order to analyze the role of nonequilibrium effects. Namely, within collision theory, the rate of chemical reaction (2) can be described as:

\[ v_{ch} = \int d\tilde{c}_1 \int d\tilde{c}_2 \int d\Omega f_1 |\tilde{c}_1 - \tilde{c}_2| \sigma^* (|\tilde{c}_1 - \tilde{c}_2|) \] (3)

where \( \tilde{c}_1 \) and \( \tilde{c}_2 \) are the velocities of the molecules, \( |\tilde{c}_1 - \tilde{c}_2| \) their relative speed, \( \Omega \) the solid angle, \( f_1 \) and \( f_2 \) the velocity distribution functions (in general nonequilibrium ones) and \( \sigma^* (|\tilde{c}_1 - \tilde{c}_2|) \) is the differential cross-section of the chemical reaction. Only in the absence of nonequilibrium effects \( f \) can be written down in the form of the Maxwell–Boltzmann velocity distribution function:

\[ f^{(0)} = n \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp \left[ - \frac{mc^2}{2k_B T} \right] \] (4)
with $n$ the number density of the molecules, $m$ their mass, $k_B$ the Boltzmann constant and $T$ the temperature.

Present [2–4] introduced the following expression for the chemical reaction cross-section:

$$
\sigma_p^* (|\vec{c}_i - \vec{c}|) = \begin{cases} 
0, & \epsilon < \epsilon^* \\
\frac{d^2}{4} \left( 1 - \frac{\epsilon^*}{\epsilon} \right), & \epsilon \geq \epsilon^* 
\end{cases}, \quad (5)
$$

where $d$ is the diameter of the reacting spheres, $\epsilon$ represents the center-of-mass frame kinetic energy of two colliding spheres with relative velocity $\vec{c}_i - \vec{c} = \vec{c}_{rel}$,

$$
\epsilon = \frac{1}{4} m (\vec{c}_i - \vec{c})^2. \quad (6)
$$

and $\epsilon^*$ is the threshold energy, i.e. such an energy for two spheres that collide with a relative speed $c_{rel}$, which is characteristic of the considered reaction. The cross-section (5) is very convenient because it permits to get relatively simple and reasonable expressions. For example, after introduction of Eqs. (4) and (5) into Eq. (3), i.e. $f = f^{(0)}$, $f_1 = f_1^{(0)}$ and $\sigma_p^* (|\vec{c}_i - \vec{c}|) = \sigma_p^* (|\vec{c}_{rel}|)$, the expression for the equilibrium rate of chemical reaction is:

$$
\nu_{ch}^{(0)} = 4 \pi n^2 d^2 \left( \frac{\pi k_B T}{m} \right)^{1/2} \exp \left[ - \frac{\epsilon^*}{k_B T} \right]. \quad (7)
$$

where the pre-exponential term corresponds to the collision frequency of the moving spheres and the exponential term shows the role of the threshold energy $\epsilon^*$. As it can be shown [5], the Arrhenius activation energy $\epsilon_A$ [6] is connected to $\epsilon^*$ through the simple relationship:

$$
\epsilon_A = \epsilon^* + \frac{k_B T}{2}. \quad (8)
$$

Therefore, $\epsilon_A$ depends on the temperature and the linear Arrhenius relation of $\ln \nu_{ch}^{(0)}$ on $1/T$ is not fulfilled for the model of Present unless $k_B T/2 \ll \epsilon^*$.

It is very convenient to introduce a quantity $\eta$ describing the role of nonequilibrium effects in the following form:

$$
\eta = 1 - r = 1 - \frac{\nu_{ch}}{\nu_{ch}^{(0)}}, \quad (9)
$$

The quantity $\eta$ has been used since long ago [4] to analyze the nonequilibrium effects associated with the proceeding of the chemical reaction, which leads to the deformation of the Maxwell–Boltzmann distributions $f^{(0)}$ and $f_1^{(0)}$. The ratio $r$ is here introduced to describe the relative change of $\nu_{ch}$.

The problems dealing with different nonequilibrium effects connected with chemical reactions have been analyzed in [7–16] and many other papers.

Several years ago, Cukrowski and Popielawski [17] analyzed the effect of transport processes, such as heat and viscous flows, on $\nu_{ch}$ and therefore on $r$. It is worthwhile to mention that in Ref. [17] a minus sign in the definition (3) of $\nu_{ch}$, and therefore in the right-hand side of Eq. (7), was introduced. This does not change the relative effect, given by Eq. (9).

Cukrowski and Popielawski [17] neglected the effect of the chemical reaction on the velocity distribution function. It was possible to do so because the time scales of the processes could be chosen to be different. This condition is fulfilled for a slow chemical reaction (characterized by a large threshold energy) and a large heat flux (or a large temperature gradient). However, the temperature gradient cannot be too large in order to analyze a system in the hydrodynamic region (not in the Knudsen region, in which the mean free path would be too large) [18, 19].

The authors of [17] also assumed that the effect of the heat flux and/or the pressure tensor can be taken into account by making use of the linear approximation. They therefore wrote down the distribution function as $f \approx f^{(0)} [1 + \phi^{(1)}]$, where the perturbation $\phi^{(1)}$ can be found out by means of the Chapman–Enskog or Grad kinetic theory methods, and is due to the presence of a nonvanishing heat flux and/or pressure tensor in the system. Under these assumptions, they came to the conclusion that the presence of a heat flux and/or pressure tensor can modify the rate of chemical reaction. In the present paper we denote their $r$ by $r^{(1)}$ because, as we have recalled, they assumed the linearity $f \approx f^{(0)} [1 + \phi^{(1)}]$. As it was stated in [17], the procedure followed in that paper should be regarded as a first approach to the problem and may not yield quantitatively reliable results. This is so because the use of an expansion of the form $f \approx f^{(0)} [1 + \phi^{(1)} + \phi^{(2)} + \cdots ]$, instead of the linear approximation $f \approx f^{(0)} [1 + \phi^{(1)}]$, into (3), will yield second-order corrections to Eq. (7) arising from $\phi^{(1)} \phi^{(1)}$ but also from $\phi^{(2)}$ and from $\phi^{(2)}$. Therefore, the role of the last two of these terms
(which were completely neglected in [17]) can be important, although their calculation in the framework of, e.g., the Burnett or Grad kinetic theory methods may be very complicated. In fact, several years ago the authors of [17] decided to take these additional terms into account, but after a discussion with Rudyak [20] during a symposium [21], the first author of Ref. [17] could see that a kinetic-theoretical approach to this problem would be too complicated. We think that the information theory approach to nonequilibrium statistical mechanics, which is based on the maximum entropy principle [22–24] and plays an important role in some developments of extended irreversible thermodynamics [25–28], is another reasonable possibility for the evaluation of $\phi^{(2)}$, and therefore to evaluate an additional term in $r$ [see Eq. (9)], which we denote $r^{(2)}$. We would like to stress that the motivation of the present paper is to find out this correction to the results in [17], that this is a problem of chemical kinetics, and that the use of information theory in the present paper is justified only as one tentative possibility to cope with it.

Nettleton and Torrisi [29] discussed the possibility of using extended irreversible thermodynamics for the analysis of the coupling of heat flow to a unimolecular reaction (see also [30]). Recently, Nettleton [31,32] has made use of information statistical theory and extended thermodynamics (see also Refs. [33], [34] and [27]) to analyze the nonequilibrium flow-dependent corrections to the chemical rate constant in gases.

The aim of this paper is to make use of information theory in order to evaluate the additional terms (mentioned above) and to calculate the ratio $r^{(2)}$ connected with these additional terms, to compare $r^{(2)}$ with $r^{(1)}$ (obtained from the linearized theory, as mentioned above), as well as to compare the total $r^{(1)} + r^{(2)}$ with $r^{(1)}$, in order to see the role of the influence of the heat flux on the rate of chemical reaction.

The paper is organized as follows. In Section 2 we begin with a brief explanation on information theory. We then recall some information-theoretical results that are due to other authors, and that allow to write down an expression for the velocity distribution function that includes nonequilibrium terms up to second order in the heat flux. In Section 3 we use this distribution function for the derivation of the analytical expressions for the nonequilibrium effects of the heat flux on the rate of chemical reaction. In Section 4 we present numerical evaluations of these nonequilibrium effects. In Section 5 we discuss the meaning of our new results, they are compared with those obtained from the linearized Boltzmann equation [17] and with those recently derived by Nettleton [31], and we also give some concluding remarks.

2. Information theory

As already mentioned in the introduction, information theory is here not analyzed but only used as a helpful tool in the description of the velocity distribution function. We are aware that the applicability of information theory to nonequilibrium statistical mechanics is not unanimously accepted. However, since we have decided to use this theory, we will briefly characterize it below.

In the case of thermodynamic equilibrium, the most probable velocity distribution function for a classical non-relativistic monatomic ideal gas is the Maxwell–Boltzmann distribution. A detailed statistical approach for this case has been discussed by many authors, see specially Ref. [35]. Such a probabilistic procedure was extended to nonequilibrium systems by many authors, specially by Jaynes [23]. Jaynes noted that, both in equilibrium and outside equilibrium, the mathematical theory of communication allows to interpret the entropy density as a measure of that information on the microstate of the system that is not contained in the distribution function. By maximizing the entropy density, this author obtained the maximum of such an information. In this way it is possible to get the most probable nonequilibrium velocity distribution for a given macrostate. The procedure consists in maximizing the entropy density under the set of constraints that fix the macrostate (which may include, e.g., the existence of a given heat flux) [22]. It is worth to comment that, at first sight, this method might seem inconsistent since, according to the second law, it is in equilibrium that the entropy of an isolated system reaches its maximum. However, if we maximize the entropy density under a set of macroscopic constraints, including, e.g., the constrain of a given, prescribed, non-vanishing heat flux, we are in fact comparing different nonequilibrium distribution
functions that correspond to a given, prescribed nonequilibrium macrostate (and not to several equilibrium and nonequilibrium states) and choosing the most probable one, so that there is no inconsistency with the second law. This widely-used approach (see [22–28] and references therein) has been recently applied by Domínguez and Jou [36], who have proposed an explicit expression for the distribution function of an ideal gas at rest under a heat flux. By maximizing the entropy density, i.e. \( \rho s = -k_B \int d\tilde{c}f \ln f \), under the constraints of prescribed particle number density, \( n = \int d\tilde{c}f \), vanishing barycentric velocity, \( \dot{0} = j d\tilde{c}mc \tilde{f} \), and prescribed internal energy density and heat flux, \( \rho u = j d\tilde{c}c^2_3(mc^2)\tilde{f} \) and \( \dot{q} = j d\tilde{c}c^2_3(mc^2)\tilde{f} \), respectively, one finally finds, up to second order in \( \tilde{q} \) (see equation (30) in Ref. [36]):

\[
f = \frac{1}{Z} \exp \left[ -\beta \frac{1}{2} mc^2 \right] \left[ 1 - \left( \frac{1}{2} mc^2 - \frac{5}{2\beta} \right) \tilde{\gamma} \cdot \tilde{c} \right]
+ \frac{1}{2} \left( \frac{1}{2} mc^2 - \frac{5}{2\beta} \right)^2 \left( \tilde{\gamma} \cdot \tilde{c} \right)^2,
\]

(10)

where the Lagrange multipliers \( \beta \) and \( \tilde{\gamma} \) respectively are given by

\[
\beta = \frac{1}{k_B T},
\]

(11)

\[
\tilde{\gamma} = -\frac{2}{5} \frac{m}{nk_B T^3} \tilde{q},
\]

(12)

where \( T \) is the thermodynamic temperature, i.e. \( T^{-1} = \partial s/\partial u \) (in Ref. [36], the distribution function is written in terms of the kinetic temperature \( T_K \), which satisfies \( \frac{2}{3} nk_B T_K = \rho u \)); in the present paper we use the notation in Refs. [26,27,29–34], whereas in some studies, see e.g. [36,25], the symbol \( \theta \) is used in the place of \( T \), and \( T \) is used instead of \( T_K \). Eq. (12) is valid up to second order in \( \tilde{q} \).

The partition function \( Z \) appearing in Eq. (10) can be found out from the constraint of prescribed particle number density, i.e. from the normalization of the distribution function:

\[
n = \int d\tilde{c}f,
\]

(13)
important topic and it deserves further consideration in the future.

3. Calculation of the reaction rate

After taking into account Eq. (15) we can write Eq. (3) as:
\[ v_{ch} = v_{ch}^{(0)} + v_{ch}^{(1)} + v_{ch}^{(2)} , \]
where \( v_{ch}^{(i)} \) refers to terms of order \( i \) in \( q \), i.e. \( i = 0 \) for \( q^0 \), \( i = 1 \) for \( q^1 \) and \( i = 2 \) for \( q^2 \),
\[ v_{ch}^{(0)} = \int d\vec{c} \int d\vec{c}_1 \int d\Omega f^{(0)} f^{(0)} |\vec{c}_1 - \vec{c}| \sigma^* (|\vec{c}_1 - \vec{c}|) , \]
\[ v_{ch}^{(1)} = \int d\vec{c} \int d\vec{c}_1 \int d\Omega f^{(0)} f^{(1)} ( \phi_1^{(1)} + \phi_1^{(0)}) |\vec{c}_1 - \vec{c}| \]
\[ + \sigma^* (|\vec{c}_1 - \vec{c}|) , \quad (21) \]
and
\[ v_{ch}^{(2)} = v_{ch}^{(2a)} + v_{ch}^{(2b)} + v_{ch}^{(2c)} , \]
with
\[ v_{ch}^{(2a)} = \int d\vec{c} \int d\vec{c}_1 \int d\Omega f^{(0)} f^{(0)} \phi_1^{(1)} |\vec{c}_1 - \vec{c}| \]
\[ + \sigma^* (|\vec{c}_1 - \vec{c}|) , \quad (24) \]
\[ v_{ch}^{(2b)} = \int d\vec{c} \int d\vec{c}_1 \int d\Omega f^{(0)} f^{(0)} \left[ \phi_1^{(2)} + \phi_1^{(0)} \right] |\vec{c}_1 - \vec{c}| \]
\[ + \sigma^* (|\vec{c}_1 - \vec{c}|) , \quad (25) \]
\[ v_{ch}^{(2c)} = \int d\vec{c} \int d\vec{c}_1 \int d\Omega f^{(0)} f^{(0)} \left[ \phi_1^{(1)} + \phi_1^{(0)} \right] |\vec{c}_1 - \vec{c}| \]
\[ + \sigma^* (|\vec{c}_1 - \vec{c}|) . \quad (26) \]

It is worthwhile to observe that in previous studies [17,39], which where based on the linearized Boltzmann equation, the term \( \phi^{(2)} \) was not considered. Therefore, it was possible to take the last two terms in Eq. (23) into account, although it is necessary to do so because they are of the same order as the first term. These last two terms in Eq. (23) play a fundamental role in the present paper.

In order to perform the integrations in Eqs. (21), (22), (24)–(26) we change from the velocities \( \vec{c} \) and \( \vec{c}_1 \) into the usual variables \( \vec{c}_{ch} = \vec{c}_1 - \vec{c} \) and \( \vec{c}_{cm} = \frac{1}{4}(\vec{c}_1 + \vec{c}) \).

As far as Eq. (22) is concerned, it is clear from Eq. (16) that \( \phi_1^{(1)} \) and \( \phi_1^{(0)} \) are odd functions of \( \vec{c} \) and \( \vec{c}_1 \), respectively. Thus after integrations we get \( v_{ch}^{(1)} = 0 \).

The calculation of \( v_{ch}^{(2)} \) can be carried out in the same way as that leading to Eq. (7). However, the calculations are rather tedious, so we will give some partial results. After making use of Present’s cross-section (5) and performing the integrations in Eqs. (24)–(26) we finally arrive at:
\[ v_{ch}^{(2a)} = \frac{4d^2 m}{75k_B^3 T^2} \left( \frac{\pi k_B T}{m} \right)^{1/2} \vec{q} \cdot \vec{q} \exp \left[ - \frac{e^*}{k_B T} \right] \]
\[ \times \left[ - \frac{e^*}{k_B T} + \frac{9}{2} \left( \frac{e^*}{k_B T} \right)^2 \right] \frac{3}{4} \left( \frac{e^*}{k_B T} \right) , \quad (27) \]
\[ v_{ch}^{(2b)} = - \frac{8d^2 m}{5k_B^3 T^2} \left( \frac{\pi k_B T}{m} \right)^{1/2} \vec{q} \cdot \vec{q} \exp \left[ - \frac{e^*}{k_B T} \right] , \]
\[ v_{ch}^{(2c)} = \frac{4d^2 m}{75k_B^3 T^2} \left( \frac{\pi k_B T}{m} \right)^{1/2} \vec{q} \cdot \vec{q} \exp \left[ - \frac{e^*}{k_B T} \right] \]
\[ \times \left[ \left( \frac{e^*}{k_B T} \right) + \frac{13}{2} \left( \frac{e^*}{k_B T} \right)^2 \right] \frac{341}{8} \left( \frac{e^*}{k_B T} \right) . \quad (29) \]

It is worthwhile to observe that in Ref. [17] an error appeared and the coefficients 9/2, –9/4 and –3/8 in Eq. (27) in the present paper were written in a wrong way. However, the results in [17] were discussed for large values of \( e^* / k_B T \) and for this reason the term \( \left[ e^* / k_B T \right] \) was the dominating one. This lead practically to good estimations and conclusions. Therefore, we will not here include new figures for the estimation of the ratio \( r^{(1)} = (\rho_{ch}^{(2a)}) / (\rho_{ch}^{(0)}) \), which is easy to calculate from Eqs. (27) and (7), because the old ones are practically good for comparisons to be performed.

Insertion of Eqs. (27)–(29) into Eq. (23) yields the final result for the first non-vanishing correction.
to the reaction rate due to the presence of the heat flux:
\[
v_{\text{ch}}^{(2)} = \frac{4}{75} \frac{d^2 m}{k_b T^2} \left( \frac{\pi k_b T}{m} \right)^{1/2} \tilde{q} \cdot \tilde{q} \exp \left[ -\frac{\epsilon^*}{k_b T} \right] \times \left( 11 \left( \frac{\epsilon^*}{k_b T} \right)^2 + 19 \left( \frac{\epsilon^*}{k_b T} \right) + \frac{49}{4} \right). \tag{30}
\]

Eq. (30) is the fundamental equation we have been looking for. We use this equation for numerical estimations in the next section.

4. Numerical estimations

The relative non-equilibrium correction (30) for the case considered, with respect to the equilibrium reaction rate (7), is:
\[
r^{(1)} + r^{(2)} = \frac{v_{\text{ch}}^{(2)}}{v_{\text{ch}}^{(0)}} = \frac{m}{75n^2 k_b T} \tilde{q} \cdot \tilde{q} \left( 11 \left( \frac{\epsilon^*}{k_b T} \right)^2 \right) + 19 \left( \frac{\epsilon^*}{k_b T} \right) + \frac{49}{4}, \tag{31}
\]

with
\[
r^{(2)} = \frac{v_{\text{ch}}^{(2b)} + v_{\text{ch}}^{(2c)}}{v_{\text{ch}}^{(0)}}.
\]

We now perform some estimations of the influence (31) of the heat flux on the reaction rate. As in Ref. [17], we substitute the following values of the relevant parameters: \(m = 10^{-26}\) kg, \(T = 300\) K, \(n = 2.687 \times 10^{25}\) molecules/m\(^3\) (so that the pressure is 1 atm) and \(\epsilon^*/k_b T = 10\). For a heat flux of \(q = 10^5\) W/m\(^2\) the correction is only of the order of \(10^{-5}\).

Thus such an estimation leads to a very small value of this effect. However, for the same parameters as above and a flux of \(q = 10^7\) W/m\(^2\) the correction is already of 0.34 or 34%. For \(\epsilon^*/k_b T = 100\) and \(q = 10^6\) W/m\(^2\) the correction is of 29%. We think that it may be illustrative to perform estimations also in terms of the temperature gradient, since it is usually easier to measure experimentally than the heat flux. In order to perform these estimations, let us first consider the first-order velocity distribution function within information theory:
\[
f \approx f^{(0)} \left[ 1 + \phi^{(1)} \right], \tag{32}
\]

with \(f^{(0)}\) and \(\phi^{(1)}\) given by Eqs. (4) and (16). This distribution function is exactly the expression obtained in Grad’s 13-moment method (see, e.g., [25,40]) for a fluid at rest with vanishing viscous pressure tensor. Insertion of this distribution function into the steady-state Boltzmann equation yields, as it is well known [25,40], the Fourier law of heat conduction:
\[
\tilde{q} = -\lambda \nabla T, \tag{33}
\]

where \(\lambda\) is the thermal conductivity coefficient. For the model of hard spheres, according to Refs. [40] or [37] we have:
\[
\lambda = \frac{75}{64} \frac{k_b}{d^2} \sqrt{\frac{k_b T}{\pi m}}. \tag{34}
\]

In the problem considered in the present paper, we have seen that it is necessary to make use of the second-order distribution function (15) instead of the first-order one (32). The above procedure [40] can be generalized. We mean that instead of Eq. (32), Eq. (15) can be used. Eqs. (15)–(19) and (4) [instead of Eqs. (32), (4) and (16)] should be inserted into the steady-state Boltzmann equation in this case. Then additional terms would be obtained in the Fourier law (33). It is straightforward to see that some of these new terms depend on the spatial derivatives of the components of the heat flux. Since we are interested in estimating the order of magnitude of the effect, we will neglect such terms by assuming a uniform heat flux, i.e. \(\partial q_i/\partial x_i = 0\) for all values of \(i\) and \(k\). Then Eq. (33) is generalized into an expression which has the form:
\[
q_i = -\lambda \frac{\partial T}{\partial x_i} + O(q^3), \tag{35}
\]

where \(O(q^3)\) stands for a (presumably small) correction to Fourier’s law depending on the square and higher powers of the components of \(\tilde{q}\). This correction can be found out explicitly, but we will not derive it here because it is irrelevant for our problem. We can see this by noting that the dependence of the nonequilibrium correction (31) on the heat flux is of the form \(\tilde{q} \cdot \tilde{q} = \sum_i q_i^2\). On the other hand, according to Eq. (35) we have that \(q_i\) and \(\lambda \partial T/\partial x_i\) are of the same order of magnitude, and we can thus write:
\[
\tilde{q} \cdot \tilde{q} = \sum_i \left( \lambda \frac{\partial T}{\partial x_i} \right)^2 + O(q^3). \tag{36}
\]
where the $O(q^3)$ correction arises from the non-linear correction to the Fourier law in Eq. (35). It would be inconsistent to include such a correction, because Eq. (31) itself has been calculated including only terms up to second order. Therefore, Eq. (31) may be written as:

$$r^{(1)} + r^{(2)} = \frac{\nu_{ch}^{(2)}}{\nu_{ch}^{(0)}} = \frac{m}{75n^2k_BT^3} \lambda \frac{\bar{V}^T \cdot \bar{V}^T}{T} \left( 11 \left[ \frac{\epsilon^*}{k_B T} \right]^2 + 19 \left[ \frac{\epsilon^*}{k_B T} \right] + \frac{49}{4} \right). \quad (37)$$

We finally introduce two equations into Eq. (37):

$$\nu_{ch}^{(2)} / \nu_{ch}^{(0)}$$

Fig. 1. Variation of the ratio $\nu_{ch}^{(2)} / \nu_{ch}^{(0)}$ (in percent), calculated from Eq. (39), as a function of $\epsilon^* / k_B T$, for a dimensionless temperature gradient of value $(l/T)(\bar{V}^T)$ = 0.011. For $T = 300$ K, $n = 2.687 \times 10^{23}$ molecules/m$^3$ and $d = 10^{-10}$ m, this value corresponds to a temperature gradient of $3.9 \times 10^9$ K/m.

$$\nu_{ch}^{(2)} / \nu_{ch}^{(0)}$$

Fig. 2. Variation of the ratio $\nu_{ch}^{(2)} / \nu_{ch}^{(0)}$ (in percent) as a function of the dimensionless temperature gradient $(l/T)(\bar{V}^T)$ (for $\epsilon^*/k_B T = 10, 40$ and 100) calculated from Eq. (39).

Eq. (34) and the following equation for the mean free path $l$ [37],

$$l = \frac{1}{\sqrt{2\pi} nd^2}. \quad (38)$$

This yields the following expression:

$$r^{(1)} + r^{(2)} = \frac{\nu_{ch}^{(2)}}{\nu_{ch}^{(0)}} = \frac{75\pi}{2048} \left( \frac{l}{T} \right)^2 \left( 11 \left[ \frac{\epsilon^*}{k_B T} \right]^2 + 19 \left[ \frac{\epsilon^*}{k_B T} \right] + \frac{49}{4} \right). \quad (39)$$

In order to make some estimations, let us assume the values $T = 300$ K, $n = 2.687 \times 10^{23}$ molecules/m$^3$ (as before) and $d = 10^{-10}$ m. Then Eq. (39) yields, for $\epsilon^*/k_B T = 10$, an effect of 0.1% for $|\bar{V}^T| = 10^6$
K/m and of 11.7% for $|\nabla T| = 10^7$ K/m. For $\varepsilon^*/k_B T = 100$, the effect is of 10% already for $|\nabla T| = 10^6$ K/m. In Figs. 1 and 2 we plot the effect (39) as a function of the dimensionless temperature gradient $(T/1)^{-1}|\nabla T|$ and of $\varepsilon^*/k_B T$.

5. Discussion and concluding remarks

As mentioned in the introduction, many previous papers have made use of Present’s cross-section (5) in order to study different nonequilibrium effects on the rate of chemical reaction. Most of the effects (both on the reaction rate and on transport coefficients) have been predicted to be negligible, unless fast reactions are considered [i.e., unless $\varepsilon^*/k_B T$ is small; see Eq. (7)]: most of the predicted effects are negligible for $\varepsilon^*/k_B T > 5$ [41–43,11]. Such results are easy to understand even intuitively, since only fast enough reactions deform the distribution function appreciably. It should be emphasized that we have analyzed here slow reactions. Slow reactions cause negligible effects of deformation on the velocity distribution function. Such a deformation exists in our case, but it is an effect due to the large temperature gradient only. We have shown that, for a given value of the temperature gradient, the effect is higher the slower the chemical reaction is (see Fig. 1).

We have shown that in the evaluation of the nonequilibrium effect of the heat flux on the rate constant of a bimolecular chemical reaction additional terms $\mu^{(2)}$ (in Ref. [17] only terms $\mu^{(1)}$ were analyzed) can play an important role. Namely, after the expansion of the velocity distribution functions $f$ and $f_1$ in forms $f = f^{(0)}[1 + \phi^{(1)} + \phi^{(2)} + \cdots]$ and $f_1 = f_1^{(0)}[1 + \phi_1^{(1)} + \phi_1^{(2)} + \cdots]$ [see Eqs. (15)–(19)] we have derived results for $\mu^{(2)}$ obtained from the terms $\phi^{(2)}$ and $\phi_1^{(2)}$ [see Eqs. (25) and (26)] in addition to the results for $\mu^{(1)}$ obtained from the ‘square terms’ $\phi^{(1)}\phi_1^{(1)}$ analyzed in Ref. [17] [see Eq. (24)]. This provides the method proposed in [17] with a sound basis, in the sense that all contributions up to second order have now been explicitly taken into account.

It has been possible to obtain results for $\phi^{(2)}$ and $\phi_1^{(2)}$ within the information theory approach, i.e. within a statistical method based on the principle of maximum entropy which is also the basic tool in possible statistical-mechanical derivations of the fundamental equations used in extended irreversible thermodynamics [25–28]. It should be emphasized that the results for $\phi^{(2)}$ and $\phi_1^{(2)}$ have been obtained within the same formalism as that recently used by Domínguez and Jou to discuss the meaning of thermodynamic pressure in nonequilibrium systems [36]. The results obtained in such a way are more general than those obtained from the linearized Boltzmann equation. If we wanted to carry out a comparison with kinetic theory, the distribution function used here could only be compared with results obtained, e.g., from the Burnett approximation in the Chapman–Enskog method of solution of the Boltzmann equation. However, the expressions for $\phi^{(2)}$ obtained within the Burnett approximation have complicated forms and are difficult to derive. They are fairly complicated even for the Maxwellian molecules [44]. An interesting possibility would be to make use of the modified moment method [45]. On the other hand, for the effect of chemical reaction on the viscosity coefficient some small differences between the results based on the Burnett approximation and on the moment method have been observed [46,39,9]. It is worthwhile to observe that also in the analysis of the effects of chemical reaction on diffusion in the Lorentz gas, results obtained from the Résoisbois perturbation method [47–49] of solution of the Boltzmann–Lorentz equation and those obtained from the moment method are different [43,50,51].

It is very interesting that the results for $\mu^{(2)}$ are of the same order of magnitude as those for $\mu^{(1)}$, but they have an opposite sign (compare Figs. 1 and 2 in this paper with figs. 3 and 4 in Ref. [17]). This means that, contrary to the decrease of the rate of chemical reaction (due to the heat flux), which was expected in Ref. [17], we have here predicted the increase of this rate, by means of an analysis that includes those terms that, in spite of being important, were omitted in [17]. When analyzing the total effect $r = \mu^{(1)} + \mu^{(2)}$ for Present’s model and for threshold energies $\varepsilon^*/k_B T$ smaller than 100, a value of the effect for $r$ of the order of 10% could be obtained at atmospheric pressure for values of the heat flux smaller than $10^7$ W/m² or for a temperature gradients smaller than $10^2$ K/m (see the estimations performed under Eqs. (31) and (39), as well as Figs. 1 and 2). Previously to our work, Nettleton [31] has already carried out
estimations of the same effect by following a different method. Making use of information theory (which has also been used here), the integrability conditions of the Helmholtz free energy and the assumption that the mean free path depends only on the molecular configuration, Nettleton [31] has been able to make estimations without assuming a specific cross-section. For the reaction $\text{D}_2 + \text{HCl} \rightarrow \text{DH} + \text{DCl}$, he obtained an effect of 1% for a heat flux of the order of $10^4 \text{ W/m}^2$ (corresponding to a temperature gradient of the order of $10^5 \text{ K/m}$), a pressure of 0.01 atm and $T = 600 \text{ K}$ (such values of the pressure and temperature correspond to a lower value of $n$ than the one considered in the previous estimations in the present paper). In order to compare his results with those presented here, let us assume these same values for the heat flux, pressure and temperature, and also $m = 10^{-28} \text{ kg}$ (which is the order of magnitude for the molecular masses in the above reaction [31]). Whereas Nettleton's results were derived without making use Present's cross-section (5), in order to make use of our results we need a value for $\epsilon^*$. For the well-analyzed pyrolysis reaction $\text{HI} + \text{H}_2 \rightarrow \text{H}_2 + \text{I}_2$ (which is the same reaction as the one already used for estimations in [17] and [52]), we have $\epsilon^* / k_\text{B} T = 37.2$ for $T = 600 \text{ K}$. Similar values for the activation energy have been measured for many reactions. Then Eq. (31) yields an effect of 2%. This result is very similar to the value of 1% estimated by Nettleton: it is very encouraging that the estimations in [31] and in the present paper agree concerning the order of magnitude of the minimum heat flux (or temperature gradient) for the effect to be appreciable. Naturally, we share the opinion of Nettleton that the effects predicted are too small to be measured in readily attainable laboratory conditions and that such effects could be studied by means of computer simulations. It may also be mentioned that in the case of strong shock waves even temperature gradients of the order of $10^8 \text{ K/m}$ appear [53–56]. However, the theoretical results here derived cannot be directly compared with experimental data obtained from shock-wave [54] or ultrasound [57] chemistry since velocity gradients are certainly very large in such situations. Thus in future work we plan to tackle the mathematically more complicated problem of the joint effect of the heat flux and the pressure tensor on the rate of chemical reaction. An analysis, similar to the one in [31], but concerning the effect of the pressure tensor, has already been presented [32]. It is also important to stress that the distribution function proposed in [38] could be used instead of the Dominguez–Jou distribution (15)–(19), and it would be very interesting to see to what extent the order of magnitude of the results is affected. We think that it is possible, in principle, that such further studies may ultimately lead to the experimental checking of theoretical predictions of the effect of dissipative fluxes on the rate of chemical reactions. But in view of the fact that this seems to require very strong nonequilibrium situations, it would be also worth to make use of computer simulations: they have already been very useful in the analysis of chemical nonequilibrium effects (see, e.g., [10], [12], [58], [14] and references therein).

It is of interest to comment briefly the dependence of the effect analyzed here on the density. In principle, the effect is higher for lower densities [see Eq. (31) or Eq. (37)]. However, as it has been stressed before [31], low densities imply that higher-order terms in the distribution function become important [59] and they also make it more difficult to measure $v_{\text{th}}^0$ itself [see Eq. (7)], unless a fast reaction were assumed, which would in turn increase the importance of the deformation in the distribution function due to the proceeding of the chemical reaction (2).

Finally, we would like to place the results in this paper into a thermodynamical, rather general perspective. After the seminal papers [60], which were the starting point of Extended Irreversible Thermodynamics, a patient search was undertaken for observable second-order effects that could provide tests for this theory. Both on the basis of extended thermodynamics and information theory [61], it was concluded that very high values of the heat flux would be necessary (more recent results support such a conclusion [38,59]; no observable at all effects are predicted for heat fluxes up to $10^8 \text{ W/m}^2$). This lead to the search for effects in which chemical reactions, in addition to heat or other fluxes, appear. In such cases the predicted effects are higher than in the absence of chemical reactions [30,29]. The present paper can thus be seen as part of the search for second-order effects, which are characteristic, from a thermodynamical point of view, of the extended theory. Because rather high values of the fluxes are
necessary even when dealing with chemical reactions ([29–32] and the present paper), and because of the problems that arise at low densities (see the previous paragraph), it has been recommended that it may be more convenient to consider such effects in liquids rather than in gases [31,32].

Just to summarize, using non-linear terms in the solution of the Boltzmann equation we have derived formulae which show that the rate of bimolecular chemical reaction in a gas phase can be fairly increased if the temperature gradient and corresponding heat flux are large.

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