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REACTION–DIFFUSION OF FOREIGN GAS — KINETIC THEORY APPROACH*

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Diffusion and reaction of a foreign gas in a carrier gas is studied in a hydrodynamic regime by means of the Boltzmann-Lorentz equation. It is assumed that the reaction is relatively slow and can be treated as a perturbation. The hydrodynamic regime of the kinetic equation is derived with the use of the Resibois perturbative method. The diffusion coefficient and reaction rate constant are calculated in the third order approximation. The coefficients contain nonequilibrium corrections resulting from the deformation of the distribution function by chemical reaction. The nonequilibrium effect of thermally activated chemical reaction is calculated for models of reactive hard spheres. This influence can be significant if molecules of the foreign gas are much lighter than those of the carrier gas.

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1. Introduction

It is well known that hydrodynamics of transfer processes and chemical kinetics of bimolecular reactions can be founded on the kinetic theory [1, 2]. As a classical result of the linear nonequilibrium thermodynamics [3], the Curie principle excludes the possibility of coupling of chemical reaction and transport processes, in the sense that linear transport coefficients are not affected by chemical reactions. This conclusion is not valid beyond the linear

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approximation. The transport coefficients for some most simple systems, like dilute gaseous mixtures, can be calculated theoretically. It is shown in this paper that the kinetic theory of gases provides also a possibility to calculate the cross effects between chemical and transfer processes in reactive gaseous systems.

The nonequilibrium effects associated with chemical reactions in gas phase have attracted a research interest for over four decades [4–7]. Most of these studies were concerned with nonequilibrium contributions to the rate constant of chemical reaction in a spatially homogeneous gaseous system. If the chemical process is relatively slow and the reaction can be treated as a perturbation, the well-known Chapman-Enskog method [1] can provide the normal solution of the appropriate Boltzmann equation. The corrections to the reaction rate are obtained from the second order approximation of the normal solution. It has been also demonstrated [6a] that this level of approximation does not predict the interaction of chemical reaction and transfer processes. Popielawski [8], and Cukrowski and Popielawski [9a] have shown that the correction to the viscosity coefficient in chemically reactive system can be obtained from the third order (Burnett) approximation of the normal solution. Such effects have been also calculated from the solution of the Boltzmann equation by the moments method [10, 11]. The modification of the Chapman–Enskog method has been recently presented [12] as an attempt to include also fast chemical processes. For intensively reactive systems this approach leads to the results essentially equivalent to that of the moment method [11, 12], but it does not extend the standard method in case of slow reactions. On the other hand, the results of the moments method and the standard Chapman–Enskog method have been found not completely coinciding [9b].

Following previous work on the quasi three-component system [13], this paper is a study of diffusion of a reactive foreign gas A in a thermalizing carrier gas C, so that the concentrations satisfy the condition

$$n_A \ll n_C \,. \tag{1}$$

Both species are involved in an irreversible chemical reaction $A + C$, the products of which can be neglected because of their low concentration. For this specific system the kinetic equations can be reduced to the single linear Boltzmann–Lorentz equation for the distribution function of the inhomogeneous, trace component. This presents an evident advantage over the regular nonlinear Boltzmann equation. For linear(ized) kinetic equations Resibois [14] developed the appealing method of derivation of the linear transport coefficients, which adopts the perturbation technique of quantum theory. It provides results equivalent to the Chapman–Enskog method, but is more convenient and transparent in calculations. In the present paper the Resibois method is applied to calculate the rate coefficient of the chemical and transfer processes, including corrections induced by the chemical reaction.

In the following section the kinetic equation for the considered system is transformed to the form appropriate for use of the Resibois method. The perturbation solution in the hydrodynamic regime is presented in Section 3. In the subsequent section, the general expression for the diffusion coefficient and the reaction rate constant is extracted from this result. It is shown that the standard Chapman–Enskog formula for the diffusion coefficient is obtained from the second order perturbation solution, while the corresponding correction due to chemical reaction appears only in the next order approximation. As a numerical example, in Section 5 the effect of chemical reaction on the diffusion coefficient and reaction rate is calculated for two models of reactive hard spheres.

2. Kinetic equation

The distribution function $f(\boldsymbol{r}, \boldsymbol{v}, t)$ of position $\boldsymbol{r}$ and velocity $\boldsymbol{v}$ of molecules of the foreign gas A at time t satisfies the modified Boltzmann–Lorentz equation [2]

$$\frac{\partial f}{\partial t} + \boldsymbol{v} \cdot \frac{\partial f}{\partial \boldsymbol{r}} = J(f) + R(f) , \tag{2}$$

where $J(f)$ is the Boltzmann–Lorentz term for collisions with the total (elastic and reactive) cross section $d\sigma$

$$J(f) = \int \left(f' f_C'^{(0)} - f f_C^{(0)} \right) \mid \boldsymbol{v} - \boldsymbol{v}_C \mid d\sigma d\boldsymbol{v}_C , \tag{3}$$

and $R(f)$ represents the correction due to the reactive collisions with the cross section $d\sigma^*$

$$R(f) = - \int f' f_C'^{(0)} \mid \boldsymbol{v} - \boldsymbol{v}_C \mid d\sigma^* d\boldsymbol{v}_C . \tag{4}$$

In Eqs (3), (4) the primed distribution functions are calculated for postcollisional velocities, and $f_C^{(0)}$ denotes the Maxwellian velocity distribution of species C at temperature T

$$f_C^{(0)}(v_C) = n_C \left(\frac{m_C}{2\pi kT} \right)^{3/2} \exp \left(- \frac{m_C v_C^2}{2kT} \right) , \tag{5}$$

Above, m_C denotes the mass of a molecule C, and k is the Boltzmann constant. (We try to simplify notation by omitting the subscript "A" for symbols referring to the species A.) Because of condition (1), the elastic collisions $A - A$ have been neglected in Eq. (2).

It is worth to note that the kinetic equation (2) is presented in a somewhat different form than it was introduced in the well-known previous studies [5–7]. The Boltzmann collisional integral J is usually calculated only for the cross section of elastic scattering. However, this differs from the corresponding cross section of the nonreactive system, because reaction is introduced in such a way that a part of elastic collisions are switched to become reactive. Consequently, it is the total cross section that is equal to the cross section of the original nonreactive system. Therefore, to obtain the collisional term of the same form as for the nonreactive system, in Eq. (3) the operator J has been appropriately complimented to account for the total cross section. This transformation results in modification of the reactive term R, which in the form of Eq. (4) constitutes the actual perturbation of the nonreactive system.

It is assumed that the inhomogeneous distribution function depends only on one spatial variable, $f(\boldsymbol{r}, \boldsymbol{v}, t = 0) = f(x, \boldsymbol{v}, t = 0)$. The collision and reaction operators, (3) and (4) respectively, retain this symmetry of the distribution. In this case, applying the Fourier transform to Eq. (2) yields the following equation

$$\frac{\partial \phi}{\partial t} + iqv_x\phi = J(\phi) + R(\phi)\,, \tag{6}$$

where ϕ is the spatial Fourier transform of the distribution function which with the above assumptions has the following form

$$\phi(q, \boldsymbol{v}, t) = \int \mathrm{e}^{-iqx} f(x, \boldsymbol{v}, t)dx\,. \tag{7}$$

The macroscopic reaction-diffusion equation is recovered from Eq. (2) in the hydrodynamic regime, in which the reaction is slow and the scale of the spatial inhomogeneities is large (relative to the mean free path of the gas molecules), and accordingly the wave vector q in Eq. (6) is small. Under these conditions, equation (6) can be treated as composed of the principal kinetic equation for the homogeneous evolution of the velocity distribution

$$\frac{\partial \phi}{\partial t} = J(\phi)\,, \tag{8}$$

and the perturbation Q formed by the reactive and convective terms

$$Q(\phi) = R(\phi) - \ iqv_x\phi\,. \tag{9}$$

The collision operator (3) is self-adjoint for the suitably defined scalar product of functions

$$\langle \chi | \phi \rangle = \int [\psi_0(v)]^{-1} \chi^*(v) \phi(v) dv . \tag{10}$$

Above, ψ_0 is the equilibrium Maxwellian velocity distribution of A

$$\psi_0(v) = \left(\frac{m}{2\pi kT} \right)^{3/2} \exp\left(-\frac{mv^2}{2kT} \right) , \tag{11}$$

which is the only stationary solution of Eq. (8). The perturbation Q is not exactly the self-adjoint operator because the convective term is anti-Hermitian. However, the simple form of this non-hermicity allows to apply the formalism for the Hermitian operators if the right and left eigenfunctions are used.

The long time behaviour of the system in the hydrodynamic regime is determined to large extent by the structure of the spectrum of the operator of Eq. (6). For hard spheres, the spectrum of the isotropic part of the nonperturbed collision operator (3) has been extensively studied [15, 16]. In particular, it is recognized that the eigenvalue $\lambda_0 = 0$ is well separated from the rest of the spectrum, which is negative. This qualitative feature should also remain for the perturbed system if only the eigenvalues are not too strongly shifted by the perturbation (9) — that means slow chemical reaction and soft spatial inhomogeneities. The basic perturbed eigenvalue λ'_0 is a small negative quantity, while the relative magnitudes of the other eigenvalues are much greater, $\lambda'_1/\lambda'_0 \gg 1$ for $i \geq 1$. In the long time limit, modes formed by the higher eigenfunctions ($i \geq 1$) decay, and the prevailing contribution to the solution of perturbed equation (6) in the hydrodynamic regime is provided by the perturbed eigenfunction ψ'_0, associated with the perturbed eigenvalue λ'_0. Hence, the hydrodynamic solution of Eq. (6) is

$$\phi(q, v, t) \simeq N_q \psi'_0(q, v) \exp(\lambda'_0 t) , \tag{12}$$

for $t \geq | \lambda'_0 - \lambda'_1 |^{-1} \simeq | \lambda'_1 |^{-1}$. Since λ'_0 is a finite negative number, the distribution function (12) steadily diminishes, because for the system with irreversible reaction there is no real stationary state which could be approached. The decay of distribution (12) is related to the depletion of the concentration of molecules

$$n_q(t) = \int \phi dv = \langle \psi_0 | \phi \rangle = N_q \exp(\lambda'_0 t) . \tag{13}$$

The irreversible reaction consumes molecules A at the steady rate whatever is their concentration. However, in the hydrodynamic mode (12) the shape of the velocity distribution is determined by the perturbed eigenfunction ψ'_0

and it remains stationary. As ψ'_0 depends on the variable q of the Fourier transform, it represents the distribution function f nonuniform in space.

3. Perturbation solution

The standard perturbation calculus can be applied to solve the equation for the basic eigenfunction

$$(J+Q)\psi'_0 = \lambda'_0\psi'_0 \,. \tag{14}$$

The eigenfunction and eigenvalue are expanded in the series

$$\psi'_0 = \psi_0 + {\psi'_0}^{(1)} + {\psi'_0}^{(2)} + \dots\,, \tag{15}$$

$$\lambda'_0 = \lambda_0 + {\lambda'_0}^{(1)} + {\lambda'_0}^{(2)} + \dots\,, \tag{16}$$

where ${\psi'_0}^{(j)}$ and ${\lambda'_0}^{(j)}$ are the j-th order perturbation contribution to ψ'_0 and λ'_0, respectively. Equations for these corrections are obtained in a usual manner by introducing expansions (15), (16) into Eq. (14) in which the perturbation Q is treated as the first order term. The familiar solutions for the contributions of the first three orders in the notation of this paper can be presented as [13]

$${\lambda'_0}^{(1)} = \langle\psi_0|Q(\psi_0)\rangle\,, \tag{17}$$

$${\lambda'_0}^{(2)} = -\langle\psi_0|QJ^{-1}\overline{Q(\psi_0)}\rangle\,, \tag{18}$$

$${\lambda'_0}^{(3)} = \langle\psi_0|QJ^{-1}\overline{QJ^{-1}Q(\psi_0)}\rangle - \lambda_0^{(1)}\langle\psi_0 \mid QJ^{-2}\overline{Q(\psi_0)}\rangle\,. \tag{19}$$

In the above equations overline denotes orthogonalization with respect to the kernel of J, which in this case is generated only by ψ_0

$$\bar{\chi} = \chi - \langle\psi_0|\chi\rangle\psi_0\,. \tag{20}$$

For the functions of the form (20) the inverse operator J^{-1} is well defined.

The eigenvalues can be expressed explicitly in terms of the reactive and convective components of the perturbation operator Q of Eq. (9). In the obtained expressions certain contributions vanish for symmetry reason. The function $\langle\psi_0 \mid$ is symmetric with respect to the inversion of v_x and can produce finite terms only when combined in the scalar product with a function of the same symmetry. The collision J and reaction R operators retain the symmetry of the transformed function in the velocity space. Consequently, the convective component iqv_x of the perturbation Q is the only factor of ${\lambda'_0}^{(j)}$ antisymmetric with respect to v_x. Evidently, only the terms which involve even number of the convective operators provide nonvanishing contributions to ${\lambda'_0}^{(j)}$. One then obtains the eigenvalues

$$
\begin{aligned}
{\lambda'_0}^{(1)} &= \langle\psi_0|R(\psi_0)\rangle\,, && (21)\\
{\lambda'_0}^{(2)} &= -\langle\psi_0|RJ^{-1}\overline{R(\psi_0)}\rangle + q^2\langle\psi_0|v_xJ^{-1}(v_x\psi_0)\rangle\,, && (22)\\
{\lambda'_0}^{(3)} &= \langle\psi_0|RJ^{-1}\overline{RJ^{-1}R(\psi_0)}\rangle - \langle\psi_0|R(\psi_0)\rangle\langle\psi_0|RJ^{-2}\overline{R(\psi_0)}\rangle\\
&\quad + q^2\Big[-\langle\psi_0|v_xJ^{-1}v_xJ^{-1}\overline{R(\psi_0)}\rangle - \langle\psi_0|v_xJ^{-1}RJ^{-1}(v_x\psi_0)\rangle\\
&\quad - \langle\psi_0|RJ^{-1}\overline{v_xJ^{-1}(v_x\psi_0)}\rangle + \langle\psi_0|R(\psi_0)\rangle\langle\psi_0|v_xJ^{-2}(v_x\psi_0)\rangle\Big]\,. && (23)
\end{aligned}
$$

Summing up Eqs (21)–(23), the eigenvalue λ'_0 in a third order approximation can be written in the form

$$\lambda'_0 = \alpha - Dq^2\,, \tag{24}$$

where α and D contain the respective terms of Eqs (21)–(23), which do not contain q or are proportional to q^2, respectively.

Using (24) in Eq. (14), the hydrodynamic regime of Eq. (6) can be written as

$$\frac{\partial\phi}{\partial t} = (\alpha - Dq^2)\phi\,. \tag{25}$$

Introducing in (25) density n_q with the use of Eq. (13), and taking the inverse Fourier transform one obtains

$$\frac{\partial n}{\partial t} = \alpha n + D\frac{\partial^2 n}{\partial x^2}\,. \tag{26}$$

4. Diffusion coefficient and reaction rate constant

Eq. (26) is the familiar reaction-diffusion equation. According to Eqs (21)–(24), the diffusion coefficient D is a sum of the second and third order terms

$$
\begin{aligned}
D^{(2)} &= -\langle\psi_0 \mid v_xJ^{-1}(v_x\psi_0)\rangle\,, && (27)\\
D^{(3)} &= \langle\psi_0|v_xJ^{-1}RJ^{-1}(v_x\psi_0)\rangle + \langle\psi_0|v_xJ^{-1}v_xJ^{-1}\overline{R(\psi_0)}\rangle\\
&\quad + \langle\psi_0|RJ^{-1}\overline{v_xJ^{-1}(v_x\psi_0)}\rangle - \langle\psi_0|R(\psi_0)\rangle\langle\psi_0|v_xJ^{-2}(v_x\psi_0)\rangle\,. && (28)
\end{aligned}
$$

The term $D^{(2)}$ is exactly the standard Chapman–Enskog result [1] — the effect of chemical reaction on diffusion is not predicted at this order of approximation. It is only the third order term which provides the correction to diffusion coefficient induced by reaction. Expression (28) is rather involved, but can be presented in a form more suitable for practical calculations. As J and R are Hermitian operators, the second component of $D^{(3)}$ is transformed as

$$\langle\psi_0|v_xJ^{-1}v_xJ^{-1}\overline{R(\psi_0)}\rangle = \langle J^{-1}(v_x\psi_0)|v_xJ^{-1}\overline{R(\psi_0)}\rangle\,. \tag{29}$$

Above term coincides with the third component of $D^{(3)}$ since

$$\langle\psi_0|RJ^{-1}\overline{v_xJ^{-1}(v_x\psi_0)}\rangle = \langle v_xJ^{-1}\overline{R(\psi_0)}|J^{-1}(v_x\psi_0)\rangle \tag{30}$$

and the scalar product is symmetric for real functions. It is also useful to put the other terms of $D^{(3)}$ in a more symmetric form

$$\langle\psi_0|v_xJ^{-1}RJ^{-1}(v_x\psi_0)\rangle = \langle J^{-1}(v_x\psi_0)|RJ^{-1}(v_x\psi_0)\rangle\,, \tag{31}$$

$$\langle\psi_0|v_xJ^{-2}(v_x\psi_0)\rangle = \langle J^{-1}(v_x\psi_0)|J^{-1}(v_x\psi_0)\rangle\,. \tag{32}$$

Eqs (27), (28) are then conveniently expressed in terms of the functions

$$\omega(v) = -J^{-1}\overline{R(\psi_0(v))}\,, \tag{33}$$

$$v_x\chi(v) = J^{-1}(v_x\psi_0(v))\,. \tag{34}$$

ω and χ are isotropic functions of $\boldsymbol{v}$, and represent the first order corrections to the eigenfunction ψ_0. Using (29)–(34) the components of the diffusion coefficient can be written in the form

$$D^{(2)} = D_{CE} = -\tfrac{1}{3}\langle\psi_0|v^2\chi\rangle\,, \tag{35}$$

$$D^{(3)} = -\tfrac{2}{3}\langle\omega|v^2\chi\rangle + \langle v_x\chi|R(v_x\chi)\rangle - \tfrac{1}{3}\langle\psi_0|R(\psi_0)\rangle\langle\chi|v^2\chi\rangle\,. \tag{36}$$

Similarly, the reaction rate α consists of three contributions of successive orders

$$\alpha^{(1)} = \langle\psi_0|R(\psi_0)\rangle\,, \tag{37}$$

$$\alpha^{(2)} = -\langle\psi_0|RJ^{-1}\overline{R(\psi_0)}\rangle = -\langle\psi_0|R(\omega)\rangle\,, \tag{38}$$

$$\begin{aligned}\alpha^{(3)} &= \langle\psi_0|RJ^{-1}\overline{RJ^{-1}R(\psi_0)}\rangle - \langle\psi_0|R(\psi_0)\rangle\langle\psi_0|RJ^{-2}\overline{R(\psi_0)}\rangle \\ &= \langle\omega \mid R(\omega)\rangle - \langle\psi_0|R(\psi_0)\rangle\langle\omega|\omega\rangle\,. \end{aligned} \tag{39}$$

The term $\alpha^{(1)}$ is a quasi-equilibrium reaction rate, calculated assuming the Maxwellian distribution. The next order terms present the corrections due to deformation of the equilibrium distribution [6, 7].

5. Reaction-diffusion for models of reactive hard spheres

To calculate coefficients (35)–(39) for particular molecular model one has to obtain ω and χ from the equations

$$J(\omega(v)) = -\overline{R(\psi_0(v))}, \tag{40}$$

$$J(v_x\chi(v)) = (v_x\psi_0(v)). \tag{41}$$

As in the standard manner of the Chapman–Enskog method, ω and χ are assumed in the form of expansions

$$\omega(v) = \psi_0 \left(a_1 S^{(1)}_{1/2}(c^2) + a_2 S^{(2)}_{1/2}(c^2) + \ldots\right), \tag{42}$$

$$\chi(v) = \psi_0 \left(b_0 S^{(0)}_{3/2}(c^2) + b_1 S^{(1)}_{3/2}(c^2) + \ldots\right), \tag{43}$$

where $S_i^{(p)}$ are the Sonine polynomials of the dimensionless velocity

$$c^2 = \frac{mv^2}{2kT}. \tag{44}$$

Equations for the coefficients a_p and b_p are obtained by taking the scalar products of Eqs (40), (41) with the appropriate Sonine polynomials. In further calculations, expansions (42), (43) were confined to the first two terms.

We apply the models of reactive hard spheres of diameters d_A and d_C for the components A and C, respectively. It is convenient to express the results in terms of the characteristic time scales related to the frequency of elastic collisions

$$(\tau_J)^{-1} = n_C d_{AC}^2 \left(\frac{8\pi kT}{\mu}\right)^{1/2}, \tag{45}$$

and reactive collisions

$$(\tau_R)^{-1} = n_C d_{AC}^2 \left(\frac{8\pi kT}{\mu}\right)^{1/2} s_f \exp(-\varepsilon), \tag{46}$$

where $d_{AC} = (d_A + d_C)/2$ is a the collisional diameter, and $\mu = mm_C/(m + m_C)$ is a reduced mass. ε and s_f denote respectively the dimensionless activation energy and steric factor for reactive collisions, explained in more detail below.

Eq. (41) does not involve chemical reaction and is the same as in the Chapman–Enskog method [1]. The scalar products for the operator J are calculated as the brackets in Ref. [1].

$$\langle \psi_0 c S_i^{(p)}(c^2) | J(\psi_0 c S_i^{(q)}(c^2)) \rangle = -\left[c S_i^{(p)}(c^2), c S_i^{(q)}(c^2)\right]_{AC}. \tag{47}$$

For hard spheres, the solution for χ in the form (43) is known

$$b_0 = -\tfrac{3}{4}\tau_J \left[M_C[1 - M_C H] \right]^{-1} , \tag{48}$$

$$b_1 = -\tfrac{3}{2}\tau_J \left[\frac{H}{M_C[1 - M_C H]} \right] , \tag{49}$$

where

$$M_A = \frac{m}{m + m_C} , \qquad M_C = \frac{m_C}{m + m_C} , \tag{50}$$

$$H = \frac{M_C}{30 - 44M_C + 27M_C^2} . \tag{51}$$

Solution of Eq. (40) requires specification of a model of chemical reaction. The reactive cross section involves the relative velocity of colliding molecules

$$\boldsymbol{g} = \boldsymbol{v} - \boldsymbol{v}_C . \tag{52}$$

Two models are considered, in which reaction takes place with the probability s_f (steric factor) if the relative velocity satisfies the following condition:

Model I. The Prigogine model [4]

$$| \boldsymbol{g} | \geq g^* . \tag{53}$$

Model II. The line-of-centers model [5a]

$$\boldsymbol{e} \cdot \boldsymbol{g} \geq g^* , \tag{54}$$

where $\boldsymbol{e}$ is the unit vector along the line connecting the centers of the reacting molecules at the instant of impact. The threshold relative velocity g^* determines the activation energy of the reaction which is defined in the dimensionless form

$$\varepsilon = \frac{\mu g^{*2}}{2kT} . \tag{55}$$

The coefficients of expansion (42) for both models can be presented in the common form

$$a_1^i = \frac{\tau_J}{4\tau_R G M_A} \left[\left(G + \tfrac{1}{2}M_C^2 \right) E_1^i + \tfrac{1}{2}M_C^2 E_2^i \right] , \tag{56}$$

$$a_2^i = \frac{\tau_J M_C}{4\tau_R G M_A} \left[E_1^i + E_2^i \right] , \tag{57}$$

where $i = I, II$ is the index of the model, and the coefficients for the respective models are

$$E_1^I = \tfrac{1}{2} + \frac{\varepsilon}{2} + \varepsilon^2 , \qquad E_1^{II} = \tfrac{1}{2} + \varepsilon , \tag{58}$$

$$E_2^I = \tfrac{1}{4} + \frac{\varepsilon}{4} + 2\varepsilon^2 - \varepsilon^3 , \qquad E_2^{II} = \tfrac{1}{4} + \varepsilon - \varepsilon^2 \tag{59}$$

and

$$G = 5 - 6M_C + 7M_C^2 . \tag{60}$$

The quasi-equilibrium reaction rate constant (37) for the above models has the form

$$\alpha_i^{(1)} = -\frac{E_0^i}{\tau_R} , \tag{61}$$

where

$$E_0^I = 1 + \varepsilon , \qquad E_0^{II} = 1 . \tag{62}$$

The lowest order correction to the reaction rate can be calculated by means of Eqs (38), (42) and (56), (57)

$$\alpha_i^{(2)} = \frac{\tau_J}{4\tau_R^2 G} \frac{m + m_C}{m} M_C \left(G \cdot (E_1^i)^2 + \tfrac{1}{2} M_C^2 (E_1^i + E_2^i)^2 \right) . \tag{63}$$

The relative correction to the reaction rate constant

$$\eta = \frac{\alpha^{(2)}}{\alpha^{(1)}} , \tag{64}$$

is presented in Fig. 1 as a function of the relative molecular mass M_A, for the activation energy $\varepsilon = 1.5$. The results presented in Figures have been calculated for a steric factor $s_f = 0.02$. The small value of s_f has been chosen in order to keep low the probability of reactive collision and ensure that the obtained results remain in the range of validity of perturbative solution. The dependence of η on the activation energy ε is plotted in Fig. 2 for the mass $M_A = 0.05$, which lies in the range of M_A where the effect is most significant. (*cf.* Fig. 1)

In terms of the expanded functions (42), (43), the effect of the chemical reaction on the diffusion coefficient, Eq. (36), is expressed in the following form

$$\begin{aligned} D_i^{(3)} = -D_{CE} \Big[& a_1^i (2 - 10H) + 10 a_2^i H + \frac{\tau_J}{\tau_R [1 - M_C H]} \Big(H^2 M_C^2 E_3^i \\ & + H M_C (2 - 11H) E_2^i + (\tfrac{1}{2} - 5H + 15H^2) E_1^i - K_i \Big) \Big] , \end{aligned} \tag{65}$$

where

$$\begin{aligned} E_3^I &= \tfrac{3}{4} + \tfrac{3}{4}\varepsilon + \tfrac{27}{2}\varepsilon^2 + 13\varepsilon^3 + 2\varepsilon^4 , \\ E_3^{II} &= \tfrac{3}{4} + \tfrac{9}{2}\varepsilon - 9\varepsilon^2 + 2\varepsilon^3 , \end{aligned} \tag{66}$$

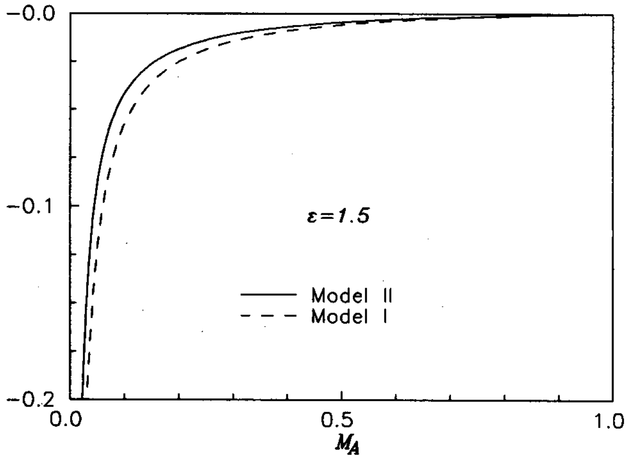

Fig. 1. The relative correction η to the reaction rate constant as a function of the relative molecular mass M_A. The dimensionless activation energy $\varepsilon = 1.5$, and the steric factor $s_f = 0.02$.

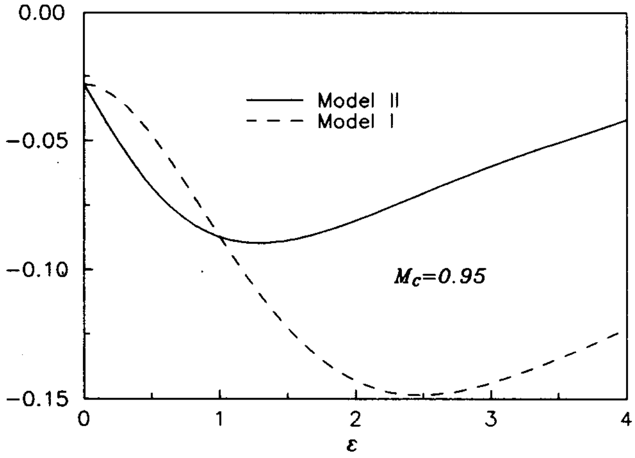

Fig. 2. The relative correction η to the reaction rate constant as a function of the dimensionless activation energy ε. The steric factor $s_f = 0.02$ and the relative molecular mass $M_A = 0.05$.

$$
\begin{aligned}
K_I &= \left(\tfrac{1}{2} + HM_C(5 - 6M_C) + H^2(15 - 30M_C + \tfrac{119}{2}M_C^2 - 38M_C^3)\right) \\
&\quad \times (2 + 2\varepsilon + \varepsilon^2) + 2HM_C^2\varepsilon^3\left(-1 + \tfrac{16}{3}H(1 - M_C) - HM_C + H\varepsilon\right) , \qquad (67)
\end{aligned}
$$

$$
K_{II} = 1 + \varepsilon HM_C(1 + \varepsilon + 4\varepsilon^2) + 4H^2M_C^2\varepsilon^3 . \qquad (68)
$$

The diffusion coefficient of reactive gases can be obtained also by means of the moment method [10, 11]. The result, when specified to the system considered, has the following form in the notation of this paper (*cf.* Eqs (69), (70) of Ref. [11])

$$D = \frac{kT}{2m}\left(\frac{\langle cS^{(1)}_{3/2}(c^2)\psi_0 \mid (J+R)(c\psi_0)\rangle^2}{\langle cS^{(1)}_{3/2}(c^2)\psi_0 \mid (J+R)(cS^{(1)}_{3/2}(c^2)\psi_0)\rangle} - \langle c\psi_0 \mid (J+R)(c\psi_0)\rangle\right)^{-1}. \quad (69)$$

It has been verified [10a, 11] that for a nonreactive system, $R = 0$, Eq. (69) provides the proper result D_{CE}. The relative correction to the standard diffusion coefficient

$$\gamma = \frac{D - D_{CE}}{D_{CE}} = \frac{D^{(3}}{D_{CE}}, \quad (70)$$

has been calculated for both models using Eqs.(65) and (69). Figure 3 presents γ for the activation energy $\varepsilon = 1$ as a function of the relative molecular mass M_A. In Figure 4 the correction γ for the molecular mass $M_A = 0.05$ is plotted vs. the activation energy ε.

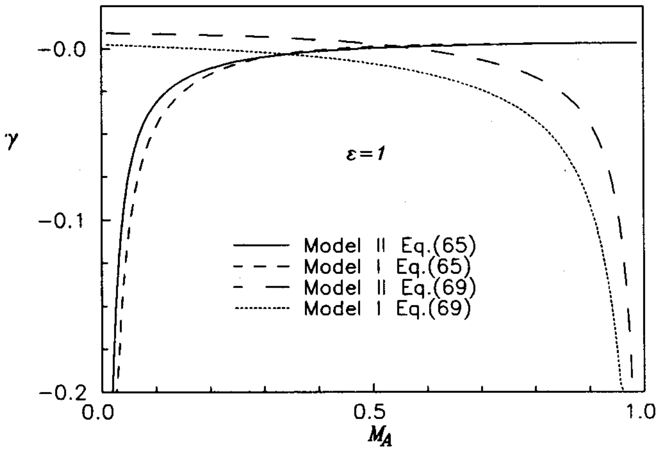

Fig. 3. The relative correction γ to the diffusion coefficient, as a function of the relative molecular mass M_A. The dimensionless activation energy $\varepsilon = 1$, and the steric factor $s_f = 0.02$.

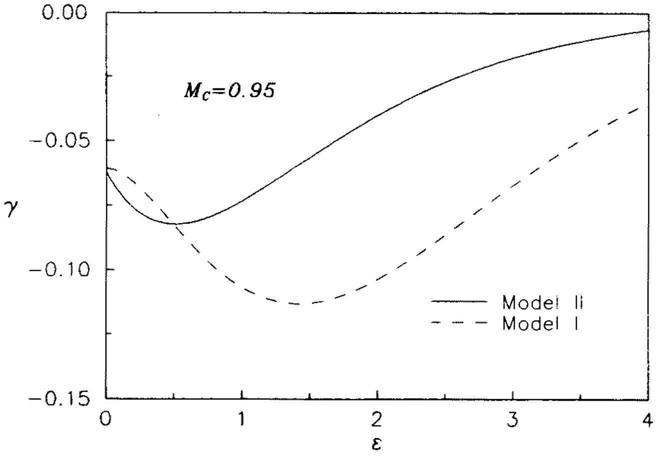

Fig. 4. The relative correction γ to the diffusion coefficient, calculated by means of Eq. (65), as a function of the dimensionless activation energy ε. The steric factor $s_f = 0.02$ and the relative molecular mass $M_A = 0.05$.

6. Discussion

Both the correction to the reaction rate constant, Eq. (63), and to the diffusion coefficient, Eq. (65), are obtained from the perturbative solution. However, while the former results from the second order approximation, one has to resort to the third order terms to calculate the latter. In this respect the Resibois method offers some conveniences in solution of the Boltzmann–Lorentz equation for the reactive foreign gas, because it allows simple formal manipulations of the otherwise involved expressions.

Application of the perturbative solution inevitably entails a question about limits of its validity. For the standard Chapman–Enskog method it is well known that this problem is not precisely resolved. The Resibois method, however, is a direct adaptation of a conventional quantum mechanical perturbation calculus, and the range of its applicability is determined by the standard requirement that a shift of eigenvalues by a perturbation is relatively small compared to separations of eigenvalues. For hydrodynamic solution (15), (16) this condition can be written as

$$| \Delta\lambda_0 | = | \lambda_0' | \ll | \lambda_1 | \; . \qquad (71)$$

The eigenvalues λ_i for the hard spheres operator are known in the literature [15], and the relation (71) can be explicitly evaluated. Since the wave vector q can be infinitesimally small, condition (71) is effective only for the reactive component of the perturbation. In particular, for the considered models it means that the steric factor s_f is sufficiently small, and its limiting value depends on the parameters M_A and ε.

The nonequilibrium corrections to the rate coefficients of transfer and chemical processes result from the deformation of the molecular velocity distribution by the chemical reaction. While the chemical reactions modeled by Eqs (53), (54) depress the high energy tail of the distribution by removing preferably faster molecules, the elastic collisions tend to restore the Maxwellian shape of the distribution. The point of balance of these both processes determines the magnitude of demaxwellization. From this point of view, presented in Figs 1, 3 dependence of the corrections on the relative mass M_A is very instructive. The effect is most significant in the Lorentz limit, $M_A \to 0$, then rapidly decays and remains relatively small for intermediate and small values of M_A. Such a slope can be explained as a result of competition between the relaxation process and chemical reaction. If the masses of molecules A and C differ substantially, the exchange of energy in elastic $A-C$ collisions is not effective. In more precise terms, times of elastic relaxation of nonequilibrium modes are longest if molecular masses of the species are disparate [15]. The mechanism of elastic scattering is then not enough efficient to restore the equilibrium velocity distribution perturbed by the chemical reaction. On the other hand however, the perturbation itself decays in the Brownian limit, $M_A \cong 1$. In this range the conditions for a reactive collision, Eqs (53), (54), effectively does not depend on the velocity v of the heavier molecule A. The probability of reaction in a single collision becomes a constant, independent of velocity. Depletion of molecules by reaction is uniform, and the shape of the velocity distribution remains nearly unperturbed. Consequently, the corrections remain small even in the Brownian limit $M_A \to 1$, despite weakening of relaxation processes. The result of the moment method [10a, 11], Eq. (69), predicts dependence quite contrary to that expected on the basis of the above qualitative arguments.

Both corrections exhibit extremes as the functions of the activation energy ε , presented in Figs 2, 4. For the correction η the largest effect can be observed around $\varepsilon = 1.5$, coinciding with the result obtained for a homogeneous system with the reaction $A + A \to$ products [7]. For higher ε the correction tapers off, because the reactive collisions become less frequent. On the other hand, for small values of ε the molecules are consumed relatively more uniformly from the whole range of velocities and the deformation of the molecular energy distribution is weaker.

Nonequilibrium effects related to chemical reaction are often explained in terms of decrease of temperature of reactants [7, 17], caused by consumption of highly energetic molecules by chemical process. Shizgal and Karplus [6b,c] recognized this effect, which may be calculated as

$$T' = T(1 - a_1), \tag{72}$$

where T' is the effective temperature of reactant. In the simplest manner, the modified rate coefficients can be calculated by introducing T' into the standard formulas for the reaction rate constant, Eq. (61), or diffusion coefficient, Eq. (35). This approach leads to satisfactory results for the correction to the reaction rate [7, 17]. However, the result obtained in this way for the diffusion coefficient provides different predictions than correction (65), as can be checked by expansion for small a_1.

The relative correction to diffusion coefficient calculated from Eq. (64) becomes positive for higher values of M_A. This result seems somewhat odd, but has been recently confirmed by computer simulations [18]. This issue will be addressed in more detail in the forthcoming paper, which will present a comparison between the analytical and numerical results.

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