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SIMPLE MODELS FOR NONEQUILIBRIUM EFFECTS IN BIMOLECULAR CHEMICAL REACTION IN A DILUTE GAS*

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Two models for reactive cross sections are introduced to analyze nonequilibrium effects connected with proceeding of the bimolecular chemical reaction $A+A \rightleftharpoons B+B$ in a dilute gas: 1. Line-of-Centers model LC, 2. the reverse model rLC leading to negative values of the Arrhenius activation energy. The perturbation method of solution of the Boltzmann equation is used to obtain analytical expressions for the rate constant of chemical reaction and for the nonequilibrium Shizgal–Karplus temperatures. It is shown that if the molar fraction of product is large enough the relative change of the rate of chemical reaction is constant, *i.e.* does not depend on the molar fraction. Replacing the equilibrium temperature by the nonequilibrium one (depending on the molar fraction) in the equilibrium equations for forward and reverse rate constants confirms these results.

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1. Introduction

Prigogine *et al.* [1,2] were the first to show that if a bimolecular reaction proceeds the nonequilibrium rate constant of chemical reaction is smaller than the equilibrium one. These authors using the perturbation method [3] of solution of the Boltzmann equation have shown that this nonequilibrium chemical effect can be large enough to be important in chemical kinetics. Present *et al.* [4,5] analyzed this effect for the line-of-centers model — very convenient because of its simplicity (further denoted as the LC model). This model was introduced in many papers [see *e.g.* Refs [6–11].

Shizgal and Karplus [12–15] discussed this problem for two cases: *(i)* for isothermal systems in which in the very beginning of chemical reaction the products can be neglected (see Ref. [1]), *(ii)* for isolated systems in which the different nonequilibrium temperatures T_A and T_B could be introduced (further analyzed as the Shizgal–Karplus temperatures or the SK temperatures).

Many authors analyzed the problem of diminishing the chemical reaction rate for various cases [16–24] Computer simulations results for the nonequilibriun rate constant [25–28], as well as the results from solutions of the sets of differential equations describing time dependence of concentrations and the nonequilibrium temperatures of components [29,30] were used to verify the results for the nonequilibrium rate constant of chemical reaction obtained from the perturbation method of solution of the Boltzmann equation. Few years ago Shizgal and Napier [31] provided a very detailed interpretation of this effect and of the SK temperatures.

2. Introductory definitions and formulation of the problems

We are interested in an analysis of this effect for the following bimolecular reaction

$$A + A \rightleftharpoons B + B \tag{2.1}$$

proceeding in a dilute gas. As this reaction proceeds the number densities n_R $(R = A, B)$ of reagents

$$n_R = \int f_R \, d\boldsymbol{c}_R \,, \tag{2.2}$$

(where f_R and $\boldsymbol{c}_R$ denote the velocity distribution function and velocity of molecules) change with time t, however, the total number density n remains constant

$$n_A + n_B = n \,. \tag{2.3}$$

The velocity v and the rate constant k for the forward reaction are defined as

$$v_{Rf} = k_{Rf} {n_R}^2 = -\frac{dn_R}{dt} = \iiint f_{R1} f_{R2} \sigma_{\mathrm{re}}^M g \, d\Omega d\boldsymbol{c}_{R1} d\boldsymbol{c}_{R2} \quad (R = A, B)\,, \tag{2.4}$$

where the subscript f denotes the forward reaction, the subscripts $R1$ and $R2$ are introduced to distinguish two colliding molecules of the same sort, σ_{re}^M is the differential reactive cross section depending on the model M (*e.g.*, analyzed in this paper $M = \mathrm{LC}$ or $M = \mathrm{rLC}$), Ω is the solid angle, whereas g is the relative velocity. In equilibrium the appropriate $v_{Rf}^{(0)}$ and $k_{Rf}^{(0)}$ can be calculated after introduction of the Maxwell–Boltzmann velocity distribution function.

$$f_R^{(0)}(T) = n_R \Big(\frac{m_R}{2\pi kT}\Big)^{3/2} \exp\left(-\frac{m_R {c_R}^2}{2kT}\right) \quad (R = A, B)\,, \tag{2.5}$$

where m_R denotes the molecular mass, k and T are the Boltzmann constant and temperature, respectively. However, for obtaining of v_{Af} it is necessary to have the nonequilibrium velocity distribution functions f_R which can be obtained from the perturbation method of solution of the appropriate Boltzmann equation [1,3]. For this reaction in nonequilibrium conditions, the total reaction rates v_A, v_B and the rate of the reverse reaction v_{Ar} are

$$v_A = v_{Af} + v_{Ar} = v_{Af} - v_{Bf} = -v_B\,. \tag{2.6}$$

For the equilibrium case these quantities are

$$v_A^{(0)} = v_{Af}^{(0)} + v_{Ar}^{(0)} = v_{Af}^{(0)} - v_{Bf}^{(0)} = -v_B^{(0)}\,. \tag{2.7}$$

The fundamental quantity (analyzed in this paper) η_R describing the nonequilibrium relative decrease of the total rate of reaction is defined as

$$\eta_R = 1 - \frac{v_R}{v_R^{(0)}} > 0\,. \tag{2.8}$$

Another important quantity is the Shizgal–Karplus nonequilibrium temperature T_R

$$T_R = \frac{2}{3}\frac{1}{n_R k} \int \frac{m_R {c_R}^2}{2} f_R \, d\boldsymbol{c}_R \quad (R = A, B)\,. \tag{2.9}$$

The temperature of system is simply related to T_A and T_B

$$T = x_A T_A + x_B T_B\,, \tag{2.10}$$

where x_A and x_B are the molar fractions.

Recently, it has also been shown [32] that in the case of isolate gaseous system the quantity η_A for the LC model can be very large. Namely, it can be even that $\eta = 45$ percent. Moreover, in the ranges of the molar fraction of product x_B in which the perturbation method of solution of the Boltzmann equation works this large effect, *e.g.* 45% is constant and does not depend on x_B (for a fast reaction x_B cannot be too small) [33]. It means that η_A does not change as the reaction proceeds. Such a possibility of constant value of η_A has been already shown in another way by Nowakowski [34]. After having obtained such a large value of η_A we decided to check it in another way. Namely, we have already shown [25,35] that the nonequilibrium values of k_{AF} can be obtained with a good approximation after replacing the temperature in the equilibrium expression for k_{Af} by the Shizgal–Karplus temperature. After introduction of the SK temperatures T_A and T_B to the equilibrium expressions k for the forward and reverse reactions we confirmed the constant value of η_A for the LC model in general and also for the case of 45% mentioned. It is interesting that the values for T_A and T_B derived in Ref. [32] could be also obtained from the formulas analyzed in Ref. [36].

However, the equations for the LC model are very simple. That is why, we decided to check the possibility of the constant value of η_A for a model leading to more complicated equations, namely for the reversed line-of-centers model (the rLC model). The rLC model was already discussed in previous papers [25, 37–42]. The rLC model is also interesting because negative values of the Arrhenius activation energy can be obtained from this model.

Our paper is organized in the following way. In Section 3 we present the formulas derived from the Boltzmann equation, in Section 4 we analyze the results for the LC model in more detailed way, in Section 5 we continue such an analysis for the rLC model, in Section 6 we summarize and discuss the results obtained.

3. Formulas obtained from the perturbation solution of the Boltzmann equation

The Boltzmann equation for the component A can be written as

$$\frac{\partial f_A}{\partial t} = I_{\rm el} + I_{\rm re}\,, \tag{3.1}$$

where the elastic and reactive terms $I_{\rm el}$ and $I_{\rm re}$ are

$$\begin{aligned} I_{\rm el} \;=\; & \iint (f'_{A1} f'_{A2} - f_{A1} f_{A2})\, \sigma_{AA} g \, d\Omega \, d\boldsymbol{c}_2 \\ & + \iint (f'_A f'_B - f_A f_B)\, \sigma_{AB} g \, d\Omega \, d\boldsymbol{c}_2\,, \end{aligned} \tag{3.2}$$

$$I_{\mathrm{re}} = \int\!\!\int (f_{B1} f_{B2} - f'_{A1} f'_{A2})\, \sigma^M_{\mathrm{re}} g \, d\Omega \, d\boldsymbol{c}_2 \tag{3.3}$$

f' denotes the distribution function after collision, σ_{AA} and σ_{AB} are the elastic differential cross sections and σ^M_{re} the reactive ones (depending on the model M which will be introduced in Sections 4 and 5 as the LC and rLC models).

As in Refs [32,33] in the reaction analyzed the molecules are assumed to be spheres which do not change their masses m and diameters d, *i.e.*

$$m_A = m_B = m \,, \tag{3.4}$$

$$d_A = d_B = d \,. \tag{3.5}$$

Therefore,

$$\sigma_{AA} = \sigma_{AB} = \frac{1}{4} d^2 \,. \tag{3.6}$$

We solve this equation by the perturbation method described by Shizgal and Karplus [12–15]. We introduce

$$f_A = f_A^{(0)}(1 + \psi_A) = f_A^{(0)} + f_A^{(1)} \tag{3.7}$$

the quantity ψ_A is expanded in the Sonine polynomials [1,3,13]

$$\psi_A = \sum_i a_A^{(i)} S_{1/2}^{(i)}(\mathcal{C}_A^2) \,, \tag{3.8}$$

where

$$\mathcal{C}_A^2 = \frac{m_A {c_A}^2}{2 k_{\mathrm{B}} T} \,. \tag{3.9}$$

We solve Eq. (3.1) within one Sonine expansion for the velocity distribution function.

$$\psi_{A1} = a_1^{(A)} S_{1/2}^{(1)}(\mathcal{C}_A^2) = a_1^{(A)} S_A^{(1)} \,, \tag{3.10}$$

where we introduce $S_A^{(1)}$ to write the first Sonine polynomial in a shorter way.

We define

$$h_{Ri}(\varepsilon^M_{\mathrm{re}}) = \frac{1}{{n_R}^2 q} \int\!\!\int\!\!\int f_{R1}^{(0)} f_{R2}^{(0)} S_R^{(i)} \sigma^M_{\mathrm{re}} g d\Omega d\boldsymbol{c}_2 d\boldsymbol{c}_1 \; (R = A, B) \quad (i = 0, 1) \,, \tag{3.11}$$

where

$$q = d^2 \left(\frac{\pi k T}{m}\right)^{1/2}, \tag{3.12}$$

$$\varepsilon_{\rm re}^M = \frac{E_{\rm re}^M}{kT}. \tag{3.13}$$

The quantities h_{Ri} depend on the model of reactive collision because $\varepsilon_{\rm re}^M$ denotes the reduced (dimensionless) value of the characteristic energy $E_{\rm re}^M$ (*e.g.* the threshold energy for the LC model)

Using the perturbation method (see Refs [13,21,32]) we can obtain

$$a_1^{(A)} = -\frac{1}{4} x_A \left(1 - \frac{x_B}{1 - x_B}\right) h_{A1}(\varepsilon_{\rm re}^M). \tag{3.14}$$

From Eqs (3.7), (3.10) and (3.14) we get the nonequilibrium value of the velocity distribution function

$$f_A = f_A^{(0)} \left[1 - \frac{1}{4} x_A \left(1 - \frac{x_B}{1 - x_B}\right) h_1(\varepsilon_{\rm re}^M) S_A^{(1)}\right]. \tag{3.15}$$

Taking into consideration Eqs (2.4), (2.6), (2.7) and (3.7) we can write

$$v_{Af} = v_{Af}^{(0)} + v_{Af}^{(1)}, \tag{3.16}$$

where

$$v_{Af}^{(0)} = \iiint f_{A1}^{(0)} f_{A2}^{(0)} \sigma_{\rm re}^M g \, d\Omega \, d\boldsymbol{c}_{A1} \, d\boldsymbol{c}_{A2}, \tag{3.17}$$

$$v_{Af}^{(1)} = \iiint \left(f_{A1}^{(0)} f_{A2}^{(1)} + f_{A2}^{(0)} f_{A1}^{(1)}\right) \sigma_{\rm re}^M g \, d\Omega \, d\boldsymbol{c}_{A1} \, d\boldsymbol{c}_{A2}. \tag{3.18}$$

In a similar way as in Ref. [13] we can obtain

$$v_{Af}^{(0)} = {n_A}^2 q h_{A0} \left(\varepsilon_{\rm re}^M\right), \tag{3.19}$$

$$v_{Af}^{(1)} = -\frac{1}{2} {n_A}^2 q \left(1 - \frac{x_B}{1 - x_B}\right) \left[h_{A1}(\varepsilon_{\rm re}^M)\right]^2. \tag{3.20}$$

We can also write

$$v_{Bf}^{(0)} = {n_B}^2 q \, h_{B0}(\varepsilon_{\rm re}^M). \tag{3.21}$$

As shown by Shizgal and Karplus [13]

$$n_A a_1^{(A)} + n_B a_1^{(B)} = 0. \tag{3.22}$$

Therefore, similarly to Eq. (3.20) we can derive

$$v_{Bf}^{(1)} = -\frac{1}{2}{n_B}^2 q \left(1 - \frac{x_A}{1-x_A}\right)\left[h_{B1}(\varepsilon_{\rm re}^M)\right]^2 . \qquad (3.23)$$

Using Eqs (2.4)–(2.7), (3.16), (3.19), (3.20) and (3.23) we get

$$v_A^{(0)} = v_{Af}^{(0)} - v_{Bf}^{(0)} = ({n_A}^2 + {n_B}^2) q \, h_{A0}\left(\varepsilon_{\rm re}^M\right) , \qquad (3.24)$$

$$v_A^{(1)} = v_{Af}^{(1)} - v_{Bf}^{(1)} = \frac{1}{2}({n_A}^2 + {n_B}^2) q \left[h_{A1}\left(\varepsilon_{\rm re}^M\right)\right]^2 . \qquad (3.25)$$

We can write the quantity η_A (see Eq. (2.8)) as

$$\eta_A = 1 - \frac{v}{v_A^{(0)}} = -\frac{v_A^{(1)}}{v_A^{(0)}} = \frac{v_{Af}^{(1)} - v_{Bf}^{(1)}}{v_{Af}^{(0)} - v_{Bf}^{(0)}} \qquad (3.26)$$

and after taking into consideration Eqs (3.24) and (3.25) in the following form

$$\eta_A(T) = \frac{1}{2}\frac{\left[h_{A1}(\varepsilon_{\rm re}^M)\right]^2}{h_{A0}(\varepsilon_{\rm re}^M)} . \qquad (3.27)$$

This fundamental quantity describing the change of the rate of chemical reaction does not depend on the molar fraction of product B, *i.e.* is constant and does not change as the reaction proceeds. We write here η_A as $\eta_A(T)$ to emphasize that this quantity depends on the temperature of system (T is constant in the reaction analyzed).

In order to confirm this independence of η_A on x_B in another way we derive the formulas for the nonequilibrium Shizgal–Karplus temperatures which can be written as [13]

$$T_R = T_R^{\rm SK} = T(1 - a_1^{(R)}) \qquad (R = A, B) . \qquad (3.28)$$

From Eqs (3.28), (3.14) and (3.22) we have

$$T_A = T\left(1 + \frac{1}{4}\frac{1-2x_B}{1-x_B} h_{A1}(\varepsilon_{\rm re}^M)\right) , \qquad (3.29)$$

$$T_B = T\left(1 + \frac{1}{4}\frac{1-2x_B}{x_B} h_{B1}(\varepsilon_{\rm re}^M)\right) . \qquad (3.30)$$

In order to get the expression for $\eta_A(T_A, T_B)$ we replace the temperature T in the formulas for $v_{Af}^{(0)}$ and $v_{Bf}^{(0)}$ (see Eqs (3.11), (3.19) and (3.21)) by the temperatures T_A and T_B, respectively

$$\eta_A(T_A, T_B) = 1 - \frac{v_A^{(0)}(T_A, T_B)}{v_A^{(0)}} = 1 - \frac{v_{Af}^{(0)}(T_A) - v_{Bf}^{(0)}(T_B)}{v_{Af}^{(0)}(T) - v_{Bf}^{(0)}(T)} \qquad (3.31)$$

and we write

$$v_{Rf}^{(0)}(T) = n_R{}^2 q\, h_{R0}\left(\frac{E_{\mathrm{re}}^M}{kT}\right) \qquad (R = A, B)\,, \tag{3.32}$$

$$\begin{aligned} v_{Rf}^{(0)}(T_R) &= n_R{}^2 q\, h_{R0}\left(\frac{E_{\mathrm{re}}^M}{kT_R}\right) \\ &= n_R{}^2 q\, h_{R0}(\varepsilon_{\mathrm{re}}^M(T_R)) \qquad (R = A, B)\,, \end{aligned} \tag{3.33}$$

where

$$\varepsilon_{\mathrm{re}}^M(T_R) = \frac{E_{\mathrm{re}}^M}{kT_R}\,. \tag{3.34}$$

It is worthwhile to observe that $\eta_A(T)$ (see Eq. (3.27) does not depend on x_B and in contrary $\eta_A(T_A, T_B)$ depends because the temperatures T_A and T_B depend on x_B (see Eqs (3.29), (3.30)). We are going to compare $\eta_A(T)$ with $\eta_A(T_A, T_B)$ for the models LC and rLC in Sections 4 and 5, respectively.

4. The line-of-centers model

We introduce in the equations for the line-of-centers model (LC)

$$\sigma_{\mathrm{re}}^M = \sigma^*, \tag{4.1}$$

which is defined as follows

$$\sigma^* = \begin{cases} 0, & g \le g^*; \\ \frac{1}{4} s_F d^2 \left(1 - \frac{g^{*2}}{g^2}\right), & g > g^*; \end{cases} \tag{4.2}$$

where s_F denotes the steric factor and the threshold relative velocity g^* is connected with the threshold energy E^*

$$E^* = \frac{m g^{*2}}{4}\,. \tag{4.3}$$

The dimensionless reduced threshold energy ε^* is introduced for the temperature T

$$\varepsilon^* = \frac{E^*}{kT}\,. \tag{4.4}$$

A similar quantity $\varepsilon^*(T_R)$ is introduced for the nonequilibrium Shizgal–Karplus temperatures T_R

$$\varepsilon^*(T_R) = \frac{E^*}{kT_R} \qquad (R = A, B)\,. \tag{4.5}$$

These definitions for the cross section (Eqs (4.1)–(4.5)) can be introduced into appropriate formulas presented in Section 3. For the quantities h (see Eqs (3.11), (3.20), (3.21), (3.32) and (3.33)) we get

$$\begin{aligned} h_{A0}(\varepsilon^*) &= 4s_F \exp(-\varepsilon^*)\,, && (4.6)\\ h_{A1}(\varepsilon^*) &= -2s_F\Big(\varepsilon^* + \frac{1}{2}\Big)\exp(-\varepsilon^*)\,, && (4.7)\\ h_{R0}(\varepsilon^*(T_R)) &= 4s_F \exp\big(-\varepsilon^*(T_R)\big) \qquad (R = A, B)\,. && (4.8) \end{aligned}$$

For $a_1^{(A)}$ (see Eq. (3.14)) we can obtain

$$a_1^{(A)} = \frac{1}{2}s_F\frac{1-2x_B}{1-x_B}\Big(\varepsilon^* + \frac{1}{2}\Big)\exp(-\varepsilon^*)\,. \tag{4.9}$$

For the reaction rates from Eqs (3.16)–(3.25) we can derive

$$\begin{aligned} v_{Af}^{(0)} &= 4{n_A}^2 s_F d^2 \left(\frac{\pi kT}{m}\right)^{1/2}\exp(-\varepsilon^*)\,, && (4.10)\\ v_{Af}^{(1)} &= -2{n_A}^2{s_F}^2 d^2\left(\frac{\pi kT}{m}\right)^{1/2}\left(1-\frac{x_B}{1-x_B}\right)\Big(\varepsilon^*+\frac{1}{2}\Big)^2\exp(-2\varepsilon^*)\,, && (4.11)\\ v_{A}^{(0)} &= 4({n_A}^2-{n_B}^2)s_F\, d^2\left(\frac{\pi kT}{m}\right)^{1/2}\exp(-\varepsilon^*)\,, && (4.12)\\ v_{A}^{(1)} &= -2({n_A}^2-{n_B}^2)s_F\, d^2\left(\frac{\pi kT}{m}\right)^{1/2}\Big(\varepsilon^*+\frac{1}{2}\Big)^2\exp(-2\varepsilon^*)\,. && (4.13) \end{aligned}$$

From Eqs (3.27), (4.6) and (4.7) we obtain the first important result for the nonequilibrium relative decrease of the rate of chemical reaction

$$\eta_{\mathrm{LC}}(T) = \frac{1}{2}s_F\Big(\varepsilon^*+\frac{1}{2}\Big)^2\exp(-\varepsilon^*)\,. \tag{4.14}$$

This decrease can be compared with such a decrease obtained from Eqs (3.31)–(3.34) (the second important result) as follows

$$\eta_{\mathrm{LC}}(T_A, T_B) = 1 - \frac{v_{Af}^{(0)}(T_A) - v_{Bf}^{(0)}(T_B)}{v_{Af}^{(0)}(T) - v_{Bf}^{(0)}(T)}\,, \tag{4.15}$$

where

$$v_{Rf}^{(0)}(T_R) = 4{n_R}^2 s_F\, d^2\left(\frac{\pi kT_R}{m}\right)^{1/2}\exp\big(-\varepsilon^*(T_R)\big) \quad (R = A, B) \tag{4.16}$$

and the nonequilibrium Shizgal–Karplus temperatures are

$$T_A = T\left[1 - \frac{1}{2}s_F\,\frac{1-2x_B}{1-x_B}\left(\varepsilon^* + \frac{1}{2}\right)\exp(-\varepsilon^*)\right], \tag{4.17}$$

$$T_B = T\left[1 + \frac{1}{2}s_F\,\frac{1-2x_B}{x_B}\left(\varepsilon^* + \frac{1}{2}\right)\exp(-\varepsilon^*)\right]. \tag{4.18}$$

As shown in Ref. [27] in the very beginning of reaction we can write

$$\frac{T_B(0)}{T} = 1 + \frac{1}{3}\left(\varepsilon^* + \frac{1}{2}\right). \tag{4.19}$$

As shown in Ref. [32] in this case the sufficient condition to avoid too large value of T_B from Eq. (4.18) is

$$x_B > \frac{0.5}{1 + \frac{1}{3s_F}\exp(-\varepsilon^*)}. \tag{4.20}$$

We emphasize again that the first result (Eq. (4.14)) does not depend on x_B and the second result (Eqs (4.15)–(4.18)) depends on x_B. In Fig. 1 we compare these results. We present $\eta_{\mathrm{LC}}(T)$ and $\eta_{\mathrm{LC}}(T_A, T_B)$ as function of the reduced threshold energy ε^*, for $x_B = 0.25$. For this value of x_B only small differences between both the results can be observed. In order to see better these differences in Figs 2 and 3 we present $\eta_{\mathrm{LC}}(T)$ and $\eta_{\mathrm{LC}}(T_A, T_B)$ as a function of x_B for three values of ε^*. Additionally, we present the ratios T_A/T, T_B/T and $T_B(0)/T$.

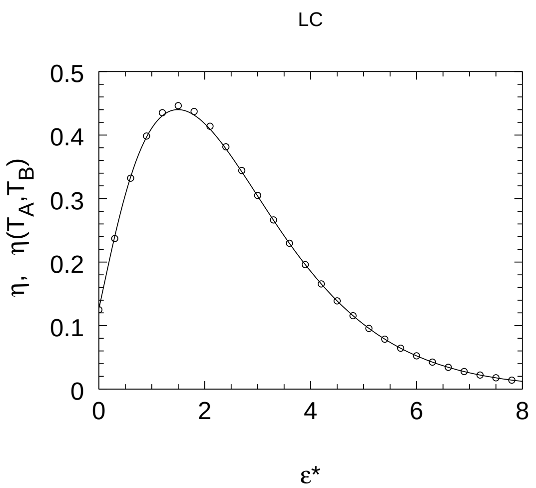

Fig. 1. Relative change of the rate constant of chemical as a function of the reduced threshold energy ε^*(see Eq. (4.4). Solid line represents η (see Eq. (4.14)) and small circles $\eta(T_A, T_B)$ (see Eqs (4.15)–(4.18)).

5. The reverse line-of-centers model

For the reverse line-of-centers model (rLC) we introduce

$$\sigma_{\rm re}^{M} = \sigma_L \,, \tag{5.1}$$

$$\sigma_L = \begin{cases} \frac{1}{4} s_F\, d^2, & g \le g_L \;, \\ \frac{1}{4} s_F\, d^2 \frac{{g_L}^2}{g^2}, & g > g_L \,, \end{cases} \tag{5.2}$$

and define the characteristic energy $E_{\rm L}$ and the reduced energies as

$$E_L = \frac{m{g_L}^2}{4} \,, \tag{5.3}$$

$$\varepsilon_L = \frac{E_L}{k_{\rm B}T} \,, \tag{5.4}$$

$$\varepsilon_L(T_R) = \frac{E_L}{kT_R} \,. \tag{5.5}$$

In this model the collisions which are reactive in the LC model become elastic and *vice versa* (see Ref. [37]). That is why we call this model the reverse line-of-centers model or shortly the rLC model. In order to present the results for the rLC model in a relatively clear way, we introduce the same numbers in equations as those in Section 4, *e.g.* the appropriate reduced dimensionless characteristic energies (see Eqs (4.4) and (4.5)) are introduced as Eqs (5.4) and (5.5). Thus, instead of Eqs (4.6)–(4.8) we introduce Eqs (5.6)–(5.8) and so on.

$$h_{A0}(\varepsilon_L) = 4s_F(1-\exp(-\varepsilon_L)) \,, \tag{5.6}$$

$$h_{A1}(\varepsilon_L) = -2s_F\left[\frac{1}{2}-\left(\varepsilon_L+\frac{1}{2}\right)\right]\exp(-\varepsilon_L) \,, \tag{5.7}$$

$$h_{R0}(\varepsilon_L(T_R)) = 4s_F \exp\left(1-\varepsilon_L(T_R)\right) . \tag{5.8}$$

The further corresponding equations derived in the same way as in Section 4 are:

$$a_1^{(A)} = \frac{1}{2}s_F\frac{1-2x_B}{1-x_B}\left[\frac{1}{2}-\left(\varepsilon_L+\frac{1}{2}\right)\exp(-\varepsilon_L)\right] , \tag{5.9}$$

$$v_{Af}^{(0)} = 4{n_A}^2 s_F d^2\left(\frac{\pi kT}{m}\right)^{1/2}\left[1-\exp(-\varepsilon_L)\right] , \tag{5.10}$$

$$v_{Af}^{(1)} = -2{n_A}^2 s_F^2 d^2\left(\frac{\pi kT}{m}\right)^{1/2}\left(1-\frac{x_B}{1-x_B}\right) \times\left[\frac{1}{2}-\left(\varepsilon_L+\frac{1}{2}\right)\exp(-\varepsilon_L)\right]^2 , \tag{5.11}$$

$$v_A^{(0)} = 4(n_A^2 - n_B{}^2) s_F\, d^2 \left(\frac{\pi k T}{m}\right)^{1/2} [1 - \exp(-\varepsilon_L)]\,, \tag{5.12}$$

$$v_A^{(1)} = -2(n_A^2 - n_B{}^2) s_F{}^2\, d^2 \left(\frac{\pi k T}{m}\right)^{1/2} \left[\frac{1}{2} - \left(\varepsilon_L + \frac{1}{2}\right)\exp(-\varepsilon_L)\right]^2 \tag{5.13}$$

We would like to emphasize that the first important result for the nonequilibrium relative decrease of the chemical reaction rate for the rLC model we obtain in a more complicate form than in Section 3 (see Eq. (4.14))

$$\eta_{\rm rLC}(T) = \frac{1}{2} s_F \,\frac{\left[\frac{1}{2} - \left(\varepsilon_L + \frac{1}{2}\right)\exp(-\varepsilon_L)\right]^2}{1 - \exp(-\varepsilon_L)}\,. \tag{5.14}$$

The second important result for comparisons is

$$\eta_{\rm rLC}(T_A, T_B) = 1 - \frac{v_{Af}^{(0)}(T_A) - v_{Bf}^{(0)}(T_B)}{v_{Af}^{(0)}(T) - v_{Bf}^{(0)}(T)}\,, \tag{5.15}$$

where

$$v_{Rf}^{(0)}(T_R) = 4 n_R{}^2 s_F\, d^2 \left(\frac{\pi k T_R}{m}\right)^{1/2} [1 - \exp\left(-\varepsilon_L(T_R)\right)]\,. \quad (R = A, B) \tag{5.16}$$

The results for the Shizgal–Karplus temperatures are

$$T_A = T\left\{1 - \frac{1}{2} s_F \,\frac{1 - 2x_B}{1 - x_B}\left[\frac{1}{2} - \left(\varepsilon_L + \frac{1}{2}\right)\exp(-\varepsilon_L)\right]\right\}, \tag{5.17}$$

$$T_B = T\left\{1 + \frac{1}{2} s_F \,\frac{1 - 2x_B}{x_B}\left[\frac{1}{2} - \left(\varepsilon_L + \frac{1}{2}\right)\exp(-\varepsilon_L)\right]\right\}. \tag{5.18}$$

Naturally, T_B can not be negative

$$T_B(0) > 0\,. \tag{5.19}$$

For the rLC model, for small values of ε_L and for small values of x_B (especially for the very beginning of reaction) the perturbation method would not work and T_B calculated from Eq. (5.18) could become negative. From Eqs. (5.18) and (5.19) it follows that the condition for x_B to avoid the problem is

$$x_B > \frac{\left(\varepsilon_L + \frac{1}{2}\right)\exp(-\varepsilon_L) - \frac{1}{2}}{\left(\varepsilon_L + \frac{1}{2}\right)\exp(-\varepsilon_L) + \frac{1}{2}}\,. \tag{5.20}$$

In Fig. 4 we present (in the same way as in Fig. 1) $\eta_{\rm rLC}(T)$ and $\eta_{\rm rLC}(T_A, T_B)$ as a function of the characteristic reduced energy ε_L for $x_B = 0.25$. In a similar way as in Figs 2 and 3 we present in Figs 5, 6 and 7 the quantities $\eta_{\mathrm{rLC}}(T)$ and $\eta_{\mathrm{rLC}}(T_A, T_B)$ as a function of x_B for three values of ε_L. Additionally, we present the results T_A/T and T_B/T in order to show that for small values of and for very small x_B (for the very beginning of reaction) negative T_B could appear.

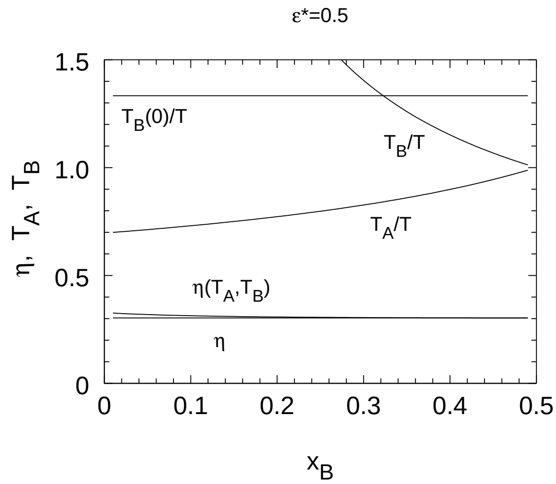

Fig. 2. Relative change of the rate constant: η (see Eq. (4.14)) and $\eta(T_A, T_B)$ (see Eqs (4.15)–(4.18)), respectively; temperatures ratios: T_A/T, T_B/T and $T_B(0)/T$ (see Eqs (4.17)–(4.19)) as a function of x_B, for the reduced threshold energy $\varepsilon^* = 0.5$.

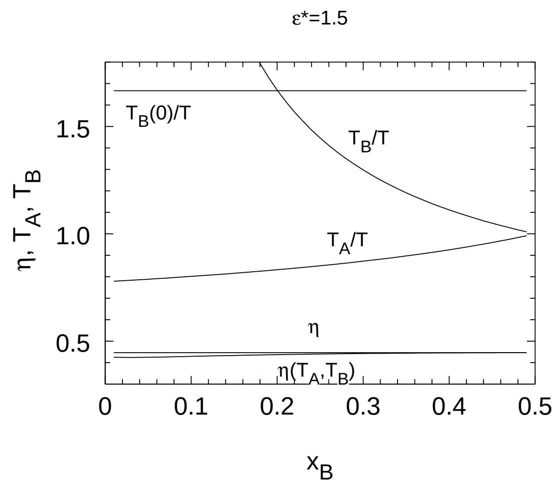

Fig. 3. The results presented as in Fig. 2 for $\varepsilon^* = 1.5$.

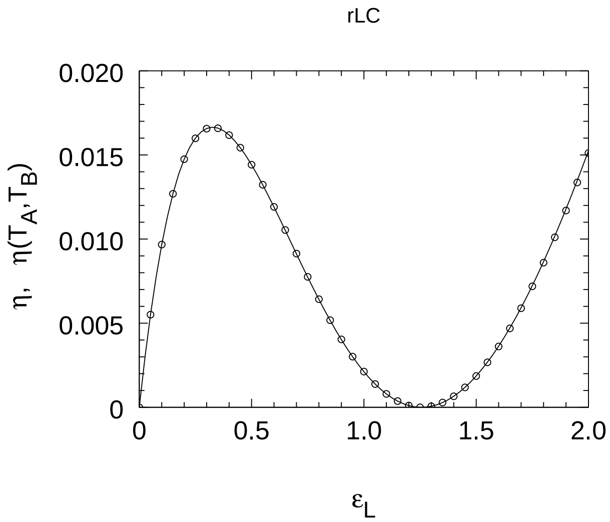

Fig. 4. Relative change of the rate constant of chemical as a function of the reduced characteristic ε_L (see Eq. (5.4)). Solid line represents η (see Eq. (5.14)) and small circles $\eta(T_A, T_B)$ (see Eqs (5.15)–(5.18)).

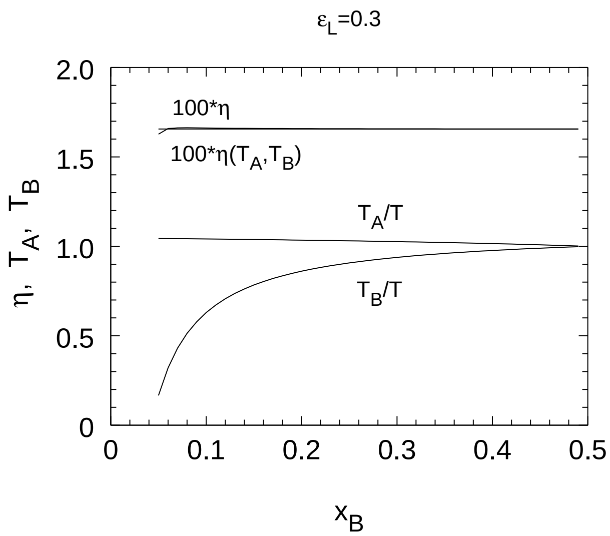

Fig. 5. Relative change of the rate constant: η (see Eq. (5.14)) and $\eta(T_A, T_B)$ (see Eqs (5.15)–(5.18)), respectively; temperatures ratios: T_A/T, T_B/T (see Eqs (5.17), (5.18)) as a function of x_B, for the reduced characteristic energy $\varepsilon_L = 0.3$.

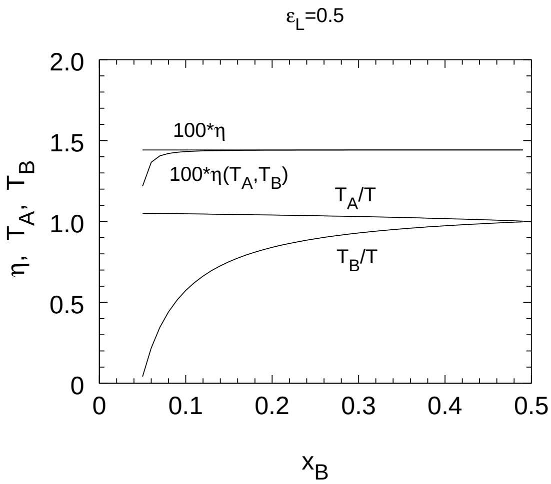

Fig. 6. The results presented as in Fig. 5 for $\varepsilon_L = 0.5$.

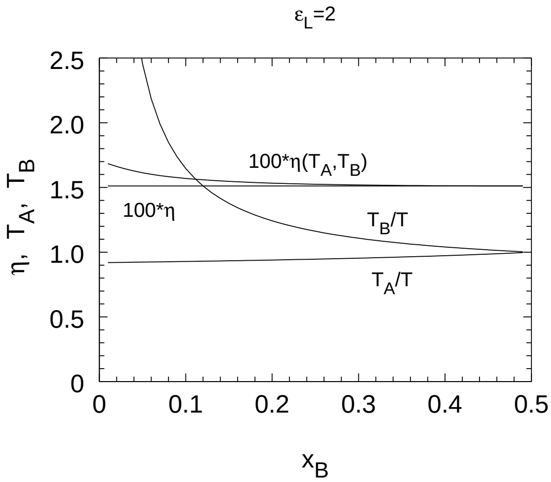

Fig. 7. The results presented as in Fig. 5 for $\varepsilon_L = 2.0$.

6. Discussion

We have analyzed the results following from the perturbation solution of the Boltzmann equation. We have obtained the results for the nonequilibrium decrease of the rate of chemical reaction directly from this solution (see $\eta_A(T)$ in Eq. (3.27)). We have also obtained such results in an indirect way. Namely, we have introduced the nonequilibrium Shizgal–Karplus temperatures (see Eqs (3.29) and (3.30)) to the equilibrium expressions for the rate constants for the reactions $A + A \to B + B$ and $B + B \to A + A$

(see $\eta_A(T_A, T_B)$, *i.e.* Eqs (3.31)–(3.34)). Such quantities η_A have been compared for two models. For the LC model Eqs (4.14), and (4.15) have been used for comparison of $\eta_{\rm LC}(T)$ and $\eta_{\rm LC}(T_A, T_B)$.

From Fig. 1 it can be seen that the decrease of the chemical reaction rate (η) can be equal even to 45 percent. We have already looked for large effects for η in the LC model [25,27]. However, as shown by Shizgal and Napier [31] our theoretical results were obtained for the system in which the forward reaction proceeded in a large excess of a second nonreactive component (with the same mass of A). Dahler [30] has stimulated us to analyze the reverse reaction too.

The differences between $\eta_{\rm LC}(T)$ and $\eta_{\rm LC}(T_A, T_B)$ are very small for $x_B = 0.25$. From Fig. 2 it can be seen that such differences for fast reaction ($\varepsilon^* = 0.5$) can be large if x_B is small. For small values of x_B the ratio T_B/T would be larger than the possible value of $T_B(0)/T$ (in the very beginning of reaction). That is why for $x_B < 0.3$ following from Eq. (4.20) the differences between the two values of η could be visible (especially for very small values of x_B), *i.e.* the perturbation method would not work because the reaction would be too fast. From Figs 2 and 3 it can be seen that the slower the reaction is (if ε^* is larger) the smaller is x_B for which these differences could be visible.

The analysis has been also performed for the rLC model for which such equations are more complicated (the Arrhenius activation energy can be negative [37,39]). It is interesting that for the rLC model the values of $\eta_{\rm rLC}(T)$ (calculated from Eq.(5.14)) as well as the values of $\eta_{\rm rLC}(T_A, T_B)$ (calculated from Eq. (5.15)) are small. That is why for this model the perturbation method works even better than for the LC model (see Figs 4, 5 and 6). In order to see the range of small values of x_B for which the perturbation method would not work for the rLC model we have presented Figs 5, 6 and 7 in the same way as Figs 2 and 3 (for the LC model). From Figs 5 and 6 it can be seen that for small values of ε_L ($\varepsilon_L = 0.3$ and 0.5) the problem with the negative T_B could appear for very small x_B (see Eqs (5.19), (5.20)). For large values of ε_L, *e.g.* $\varepsilon_L = 2$, (see Fig. 7) this problem of negative T_B does not appear.

We would like to emphasize that we are mainly interested in confirming (as in Ref. [33]) that large decrease (even 45 percent) of the rate constant of bimolecular chemical reaction can be connected with the nonequilibriun effects. This relative decrease can be constant for a large range of the molar fraction of product. One Sonine approximation is sufficient for this purpose. Introduction of the nonequilibrium Shizgal–Karplus temperatures to the equilibrium rates of forward and reverse chemical reactions confirms our results. Naturally, as shown by Shizgal and Karplus [13], for the LC model for the slow reactions in which $\varepsilon^* > 6$, more Sonine polynomials should be introduced. However, we are only interested to show that even in the case of large nonequilibrium decrease of the rate of chemical reaction η can be constant. We have analyzed the rLC model mainly to see whether, in the case of a model which can give negative values of the Arrhenius activation energy and leads to more complicated equations, such a treatment is satisfactory.

Just to summarize, we have compared, for two models, the effect of nonequilibrium relative decrease of the rate of bimolecular chemical reaction calculated directly from the perturbation solution of the Boltzmann equation with such a decrease calculated indirectly from the Shizgal–Karplus temperatures. We have confirmed and clearly shown that such a treatment permits to verify that this effect (in some cases very large and in the other small) is constant, *i.e.* does not change as the reaction proceeds.

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