

Nonequilibrium effects on the rate of bimolecular chemical reaction in a dilute gas

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Abstract

The perturbation solution of the Boltzmann equation in a dilute gas shows that the rate constant of chemical reaction $A + A \rightleftharpoons B + B$ is diminished due to nonequilibrium effects. For the line-of-centers model, the relative decrease η of the reaction rate can reach even nearly 45% (for a small reduced threshold energy ε^* and a large molar fraction x_B). For slow reactions this method is valid and η does not depend on x_B . The appropriate equilibrium expressions for reaction rate (with: (a) the temperature of the system T , (b) the nonequilibrium Shizgal–Karplus temperatures T_A and T_B) are used for this analysis. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Prigogine and Xhrouet [1] were the first to show that when in a gaseous system the bimolecular chemical reaction



proceeds, the nonequilibrium effects can diminish its rate. Namely, the nonequilibrium rate v_{Af} is smaller than the equilibrium one $v_{Af}^{(0)}$ and also the equilibrium rate constant $k_{Af}^{(0)}$ is diminished to k_{Af} . These quantities are defined as

$$v_{Af} = k_{Af} n_A n_B = - \frac{dn_A}{dt} = \int \int \int f_A f_B \sigma^* g d\Omega dc_A dc_B, \quad (2)$$

where the subscript f denotes the forward reaction, n_A and n_B are the number densities of the reagents, t is the time, f_A and f_B are the velocity distribution functions of the colliding molecules, σ^* is the differential reactive cross-section, Ω is the solid angle, whereas c_A , c_B and g are the velocities and the relative velocity, respectively. In equilibrium the appropriate $v_{Af}^{(0)}$ and $k_{Af}^{(0)}$ can be calculated after the introduction of the Maxwell–Boltzmann velocity distribution function

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

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where m_R denotes the molecular mass, k_B and T are the Boltzmann constant and temperature, respectively. A very convenient quantity $\eta_{Af} > 0$ can be defined as

$$\eta_{Af} = 1 - v_{Af}/v_{Af}^{(0)}. \quad (4)$$

The nonequilibrium velocity distribution functions f_A and f_B which are necessary for calculation of v_{Af} from Eq. (2) can be obtained from the solution of the appropriate Boltzmann equation [2,3]. The analysis of this problem has been developed by many authors [4–17].

It is interesting that the model for the cross-section σ^* plays an important role on the analytical form of f_A and f_B obtained from a solution of the Boltzmann equation. The line-of-centers model introduced by Present [4] is used very often. It is defined as

$$\sigma^* = \begin{cases} 0 & g \leq g^*, \\ \frac{1}{4} s_F d^2 (1 - g^{*2}/g^2) & g > g^*, \end{cases} \quad (5)$$

where s_F denotes the steric factor, d is the average diameter of molecules treated as spheres, g^* is the characteristic relative velocity connected with the threshold energy E^*

$$E^* = mg^{*2}/4, \quad (6)$$

where m denotes the molecular mass. The threshold energy E^* is often represented in its reduced dimensionless form

$$\varepsilon^* = E^*/k_B T. \quad (7)$$

The line-of-centers model has been used in many papers [6–11,17–34]. Present [4] solved the Boltzmann equation for the one-component reactive system $A + A \rightarrow$ products, where the products were completely neglected. He employed the Chapman–Enskog method of solution of the time-dependent Boltzmann equation [2] as used in many other papers [1,3–11,20,21,31]. This is what is referred to as the perturbation solution of the Boltzmann equation and requires that the reactive collision rate to be small relative to the elastic collision rate restoring equilibrium. The validity of the use of the Chapman–Enskog method was discussed by Shizgal [11,13] and Napier and Shizgal [27]. There are two approximations within this approach. The first is the use of the Chapman–

Enskog method and the second is the solution of the resulting steady equation with the expansion in Sonine polynomials. Shizgal and Karplus [8] reported on the rate of convergence of this expansion. Pyun and Ross [5] extended this work to multicomponent reactive systems. An important aspect of their approach is that they have constrained the temperatures of each component to be equal, in contrast to the work of Shizgal and Karplus [9,10]. These later papers form the basis of much of the work in this Letter and the previous papers [19–24,29–33] in terms of the departure of the temperatures of the different components from a common temperature. We have referred to these as the Shizgal–Karplus temperatures [21,25].

Recently, Shizgal and Napier [28] provided a very detailed interpretation of the use of the Shizgal–Karplus temperatures, and in particular the important difference between the three systems, i.e. (i) $A + A \rightarrow$ products, (ii) $A + B \rightarrow$ products, and (iii) $A + A \rightarrow B + B$. Moreover, these reactions can take place either as in isolated systems (a) or as in isothermal systems (b), i.e., in the presence of another component M in a large excess acting as a constant thermal heat bath. For the systems (i) and (ii), the products are completely neglected. The concept of different component temperatures arises naturally for the systems (ii) and (iii) because of the imposition of energy conservation [9,10] for the system and not for each component [5]. If the concentration of B in system (iii) is set to zero there is an important nonvanishing effect of vanishing product as discussed by Fitzpatrick and Desloge [12]. There are important and subtle differences in the use of Chapman–Enskog method of solution of the Boltzmann equation for these different systems arising from the imposition of energy conservation [9,10]. Shizgal and Napier also provided (see Appendix of [28]) a detailed interpretation of the work in [21,25]. The theoretical results [21] were presented for system (i) in the isolated conditions whereas Shizgal and Napier clearly showed that these authors were in fact treating the system (i) in a large excess of a second nonreactive component (with the mass of A), i.e., in the isothermal situation.

In [31] we concentrated on new problems not discussed in [28]. It should be emphasized that the

analysis was performed for a system such as the system (iii) with the introduction of the reverse reaction. We obtained new results in the isolated system for a special kind (the most simplified case) of bimolecular reaction $A + A \rightleftharpoons B + B$. This reaction was a simplified case (total neglecting of energetic effect such as a heat of reaction-associated with the changes in internal degrees of freedom) of reaction $A + A \rightleftharpoons B + B$ analyzed by Shizgal and Napier [28]. In [31] the molecules of component B could have a larger average kinetic translational energy than the molecules of component A. It was connected with choosing the appropriate reactive cross-section for which in the collisions of A with A the reactive changes were more probable for the fast molecules A which in result changed to molecules B, in contrary to the slow molecules A which could have the elastic collisions only. The reverse reaction was analyzed in the same way. Before presenting the new results (confirming some very interesting results obtained in [31]), in the next section we summarize briefly the results derived in [31].

2. Description of the actual problem and fundamental introductory equations

In [31], the nonequilibrium effects in bimolecular chemical reaction



have been analyzed and the perturbation method used for the solution of appropriate Boltzmann equation, i.e. the equation in a form:

$$\frac{\partial f_A}{\partial t} = I_{el} + I_{re}, \quad (9)$$

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

$$I_{el} = \int \int (f'_{A1} f'_{A2} - f_{A1} f_{A2}) \sigma_{AA} g \, d\Omega \, dc_{A2} \\ + \int \int (f'_{A1} f'_{B1} - f_{A1} f_{B1}) \sigma_{AB} g \, d\Omega \, dc_{B1}, \quad (10)$$

$$I_{re} = \int \int (f_{B1} f_{B2} - f'_{A1} f'_{A2}) \sigma^* g \, d\Omega \, dc_{B2}, \quad (11)$$

where f' denotes the distribution function after collision, whereas the indices A1, A2, B1, B2 are

introduced to distinguish two colliding molecules of the same sort and the elastic differential cross-section is

$$\sigma_{AA} = \sigma_{AB} = \frac{1}{4} d^2. \quad (12)$$

Eqs. (9)–(11) have been solved with the Chapman–Enskog perturbation method (which can be used if the chemical reaction is so slow that the frequency of elastic collisions is much larger than that of the reactive ones, see e.g. [11,13,27]). After adopting the Chapman–Enskog method the resulting integral equations have been solved with the expansion in Sonine polynomials. We have limited the expansion of f_A in these polynomials to the first term only

$$f_A = f_A^{(0)} \left[1 + a_1^{(A)} S_{1/2}^{(1)}(\mathcal{C}_A^2) \right], \quad (13)$$

where the coefficient $a_1^{(A)}$ is connected with the first Sonine polynomial $S_{1/2}^{(1)}(\mathcal{C}_A^2)$ (see [1,2]) has been calculated as

$$a_1^{(A)}(1) = \frac{1}{2} s_F x_A (1 - \delta_{cr} x_B^2 / x_A^2) \\ \times (\varepsilon^* + \frac{1}{2}) \exp(-\varepsilon^*), \quad (14)$$

where x_A and x_B are the molar fractions and the quantity δ_{cr} is equal to 1 (if the reverse reaction is taken into account) or to 0 (if neglected). It has been assumed that the threshold energies for the forward and reverse reactions are equal. In this special case, in the reaction (8), we do not take into account the energy connected with the internal degrees of freedom. Therefore, the temperature of system T remains constant and $dT/dt = 0$. It can be easily seen that if $\delta_{cr} = 1$, Eq. (14) simplifies to the same form as that derived in [32], however, after the additional assumption that $dT/dt = 0$. It is interesting that according to Shizgal–Karplus theory [9], the nonequilibrium temperatures of reacting components can be calculated from the expression

$$T_R^{SK}(1) = T_R(1) \\ = T \left[1 - a_1^{(R)}(1) \right] \quad (R = A, B). \quad (15)$$

We have got [31]

$$T_A^{(1)} = T \left[1 - \frac{1}{2} s_F x_A (1 - \delta_{cr} x_B^2 / x_A^2) \right. \\ \left. \times (\varepsilon^* + \frac{1}{2}) \exp(-\varepsilon^*) \right] \quad (16)$$

with

$$T = x_A T_A + x_B T_B. \quad (17)$$

We have also derived from Eq. (9) that if the reverse reaction is neglected (which corresponds to $\delta_{cr} = 0$)

$$\eta_{Af}(1) = \frac{1}{2} s_F x_A (\varepsilon^* + \frac{1}{2})^2 \exp(-\varepsilon^*). \quad (18)$$

Additionally, we have introduced the correction to the overall reaction

$$\eta_R = 1 - v_R/v_R^{(0)} \quad (R = A, B) \quad (19)$$

with the reverse reaction taken into account as v_{Ar} in

$$v_A = v_{Af} + v_{Ar} = v_{Af} - v_{Bf} = -v_B. \quad (20)$$

The quantity v_{Af} can be called also the forward reaction rate and v_A the apparent reaction rate [5]. We have derived

$$\eta_A(1) = \frac{1}{2} s_F (\varepsilon^* + \frac{1}{2})^2 \exp(-\varepsilon^*) = \eta_B(1). \quad (21)$$

This result is very interesting because, contrary to Eq. (18), the relative change of the rate of chemical reaction (8) does not depend on x_A , or equivalently on x_B . That is why we have decided to check the validity of Eq. (21) in an additional way and present the results in this Letter. For this purpose we have decided to use the Shizgal–Karplus temperatures for which the validity of use in the equilibrium rate coefficients has been already widely discussed by Shizgal and Napier [28, see p. 56; Eqs. (22–25) and Fig. 1]. Shizgal and Napier [28] demonstrated very clearly that the use of the Shizgal–Karplus temperatures in the equilibrium rate coefficient (see [28, Eq. (23)]) corresponds to the expansion of the velocity distribution function in Sonine polynomials with the expansion coefficients given by powers of a_1 (see [28, Eq. (24)]). The range of this approach was also reported and discussed.

In the particular case of reaction discussed, we have already got [31] fairly good agreement between the analytical results for the nonequilibrium Shizgal–Karplus temperatures (see Eq. (16)) and the results for temperatures obtained from the simulations [31] based on the Monte Carlo method (see, e.g. [34]). As the accuracy of the results for the rate of chemical reaction obtained from sim-

ulations is worse than in the case of the nonequilibrium temperatures, we have decided to check the validity of Eq. (21) in a different way. Namely, we will use new formulas in which the nonequilibrium Shizgal–Karplus temperatures play a fundamental role.

Our Letter is organized as follows: In Section 3 we show the theoretical results necessary for comparisons with those obtained from Eq. (21); in Section 4 we present such comparisons and in Section 5 we discuss them.

3. The nonequilibrium effect on the rate of chemical reaction

In order to calculate v_A we use the same idea as in our earlier papers [20,21]. This idea is very simple. Namely, we assume that the analytical dependence of nonequilibrium rate of chemical reaction on temperature is the same as in the equilibrium case. It means that we can write

$$v_{Rf}^{(0)} = 4s_F n_R^2 d^2 (\pi kT/m)^{1/2} \exp(-E^*/kT) \quad (R = A, B), \quad (22)$$

$$v_{Rf}(T_R) = 4s_F n_R^2 d^2 (\pi kT_R/m)^{1/2} \exp(-E^*/kT_R) \quad (R = A, B). \quad (23)$$

If we neglect the reverse reaction, after introducing the ratio of Eqs. (23) and (22) into Eq. (4) and taking into account Eqs. (7) and (16), we can write

$$\eta_{Af}(T_A) = 1 - (T_A/T)^{1/2} \exp[\varepsilon^*(1 - T/T_A)], \quad (24)$$

where from Eq. (16) we get

$$T_A = T \left[1 - \frac{1}{2} s_F x_A (\varepsilon^* + \frac{1}{2}) \exp(-\varepsilon^*) \right]. \quad (25)$$

If we do not neglect the reverse reaction we can use Eqs. (19), (20) and introduce the ratios of the appropriate nonequilibrium and equilibrium reaction rates for both the components (see Eqs. (22) and (23)). Then taking into consideration Eq. (16) with $\delta_{cr} = 1$ we can derive

$$\eta_A(T_A, T_B) = 1 - \{ n_A^2 (T_A/T)^{1/2} \times \exp[\varepsilon^*(1 - T/T_A)] - n_B^2 (T_B/T)^{1/2} \times \exp[\varepsilon^*(1 - T/T_B)] \} / (n_A^2 - n_B^2), \quad (26)$$

where

$$T_A(1) = T \left[1 - \frac{1}{2} s_F \frac{1 - 2x_B}{1 - x_B} \times \left(\varepsilon^* + \frac{1}{2} \right) \exp(-\varepsilon^*) \right], \quad (27)$$

$$T_B(1) = T \left[1 - \frac{1}{2} s_F (x_B + 1/x_B - 2) \times \left(\varepsilon^* + \frac{1}{2} \right) \exp(-\varepsilon^*) \right]. \quad (28)$$

The equations derived above are necessary to perform the comparisons desired. It should be emphasized that for derivation of these equations we decided to retain only one basis function in Eq. (13). We took into consideration that, as shown by Shizgal and Karplus [10], for small values of ε^* the convergence of the expansion in Sonine polynomials is very fast. We are mainly interested in confirming that $\eta_A(1)$ (see Eq. (21)) does not depend on x_B for the reactions with relatively small ε^* . We already used one basis function approximation in the perturbation method of solution of the Boltzmann equation [35] to solve several problems connected with simple models leading to the negative Arrhenius activation energy in the chemically reacting Lorentz gas.

4. Comparisons of the results obtained directly from the perturbation solution of the Boltzmann equation with those based on the nonequilibrium Shizgal–Karplus temperatures

We present here a few comparisons of the results for relative change η of the rate of chemical reaction calculated directly from the perturbation method (see Eqs. (4), (18), (19), (21)) with those obtained indirectly – as described in Section 3 – with the replacement of the equilibrium temperature T by the nonequilibrium ones T_A and T_B (see Eqs. (24)–(28)). Such comparisons have been already performed by Shizgal and Napier for the reaction $A + C \rightarrow$ products (see [28, Fig. 1]). For the reactions analyzed in this Letter, Fig. 1 represents such a comparison for the simplified case of neglecting of the reverse chemical reaction. The reduced threshold energy is chosen as $\varepsilon^* = 1.5$, which corresponds to the maximum nonequilib-

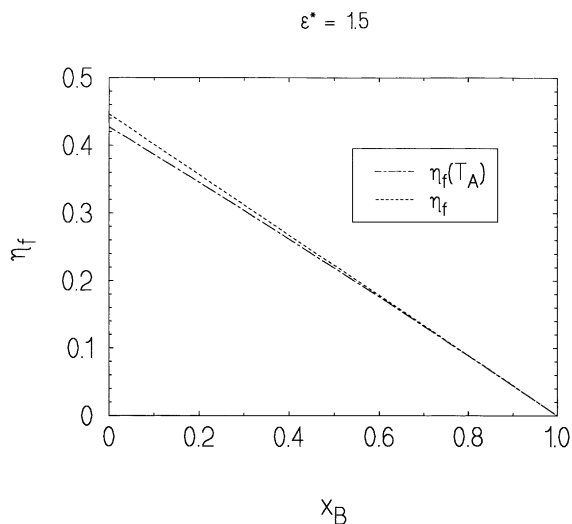


Fig. 1. Relative change of the rate constant of chemical reaction $A + A \rightarrow B + B$ represented by $\eta_f(T_A)$ (see Eq. (24)) and η_f (see Eq. (18)) as a function of x_B . The relative threshold energy and steric factor are $\varepsilon^* = 1.5$ and $s_F = 1$, respectively.

rium effect for η (compare to e.g., Fig. 2b–d). For an analysis of this result it should be taken into account that in this case the results of η , obtained from the perturbation method in the direct and indirect (introduction of T_A) ways, should be considered only for the molar fraction of product x_B fulfilling the inequality (see [31]):

$$\frac{(1 - x_B)^2}{x_B} < \frac{2 \exp(\varepsilon^*)}{3 s_F}. \quad (29)$$

This means that the comparison presented in Fig. 1 is valid for $x_B > 0.21$ only.

In the next figures we compare the results from the previously considered approach [31] and from the new one, but now without neglecting the reverse chemical reaction. Fig. 2a shows such a comparison for $\varepsilon^* = 1.5$, i.e. for the same value as that used for Fig. 1. In Fig. 2b the same comparison is presented but for a slower reaction – characterized also by $\varepsilon^* = 1.5$ but with the steric factor $s_F = 0.1$. The values of η obtained for ε^* different from 1.5 are also smaller than those shown in Fig. 2a. We present such situations for two cases: (1) a very fast reaction, e.g. $\varepsilon^* = 0$ (see Fig. 2c) and (2) a relatively slow reaction, e.g. $\varepsilon^* = 5$ (see Fig. 2d). Naturally, for analysis of re-

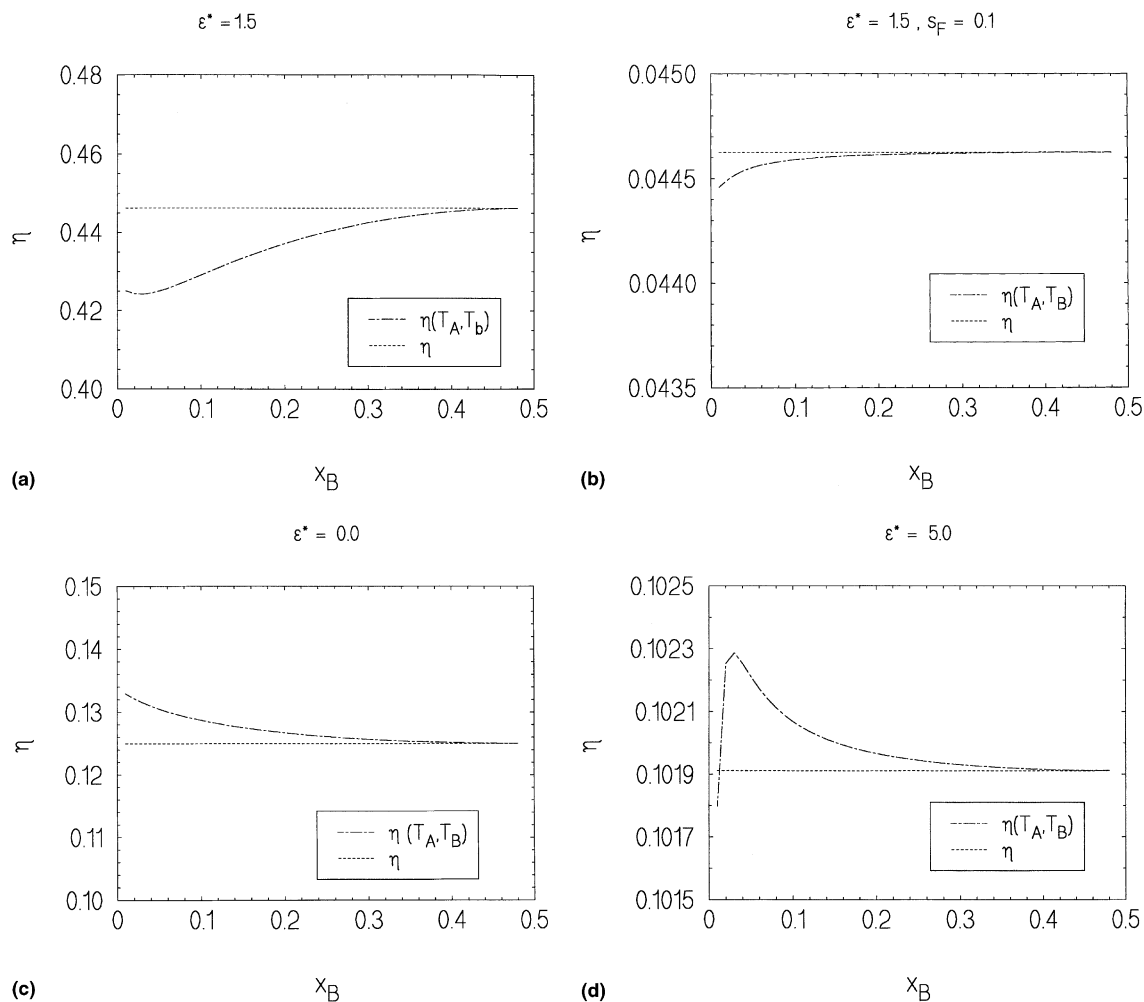


Fig. 2. Relative change of the rate constant of chemical reaction $A + A \rightleftharpoons B + B$ represented by $\eta(T_A, T_B)$ (see Eqs. (26)–(28)) as a function of x_B and compared with constant value of η (see Eq. (21)). The relative threshold energies and steric factors are: (a) $\epsilon^* = 1.5, s_F = 1$, (b) $\epsilon^* = 1.5, s_F = 0.1$, (c) $\epsilon^* = 0, s_F = 1$, (d) $\epsilon^* = 5.0, s_F = 1$.

sults presented in Figs. 2a–d the following ranges of x_B (see [31])

$$x_B > 1/[2 + (2/3) \exp(\epsilon^*)/s_F] \quad (30)$$

should be used.

5. Discussion

From Fig. 1, it can be seen that both the previously considered approach [31] (see Eq. (18)) and

the new one introduced in this Letter (see Eq. (24)) lead to nearly the same results for η_f . This provides a strong point for the validity of results in [31]. It can be also seen that the agreement is the best in the range of x_B corresponding to (0.21, 1.0), in which the reactive collision rate is small relative to the elastic one and the perturbation method should work according to Eq. (29). The maximum difference between the results obtained for η_f and $\eta_f(T_A)$ is about 3% (compare e.g., the new result $\eta_f(T_A) = 0.35$ to $\eta_f = 0.36$ from the previous ap-

proach [31]). This shows that the method based on an introduction of nonequilibrium temperatures (used already in [20,21,35]) gives reasonable results in the case of reactions analyzed in this Letter. From Figs. 2a–d it follows that also such comparisons for the values of η (see Eqs. (21) and (26)) are reasonable in the ranges described by Eq. (30). Those ranges are (0.20, 0.5), (0.031, 0.5), (0.375, 0.5) and (0.01, 0.5) for Figs. 2a–d, respectively. Therefore, these results confirm additionally the validity of such inequalities as (29) and (30). From Fig. 2a it can be seen that the maximum difference between the results for η and $\eta(T_A, T_B)$ is about 2.5% for $x_B = 0.2$ and it becomes smaller for larger values of x_B . In Figs. 2b–d, such differences are smaller. Even for a very fast reaction (analyzed in Fig. 2c) such a difference does not exceed 1% for $x_B > 0.375$. It means that $\eta(T_A, T_B)$ is nearly equal to η which is constant. This is the most valuable result following from Figs. 2a–d, because it confirms that the relative change η of the rate of chemical reaction does not depend on the concentration of product. This result has been obtained by the method described and used in this Letter.

From the results shown above we can see that the effect of nonvanishing products (emphasized already by Fitzpatrick and Desloge [12] to be not trivial) is very important because of two reasons:

1. For slow reactions, characterized by relatively large ε^* (e.g. $\varepsilon^* = 5$), the results obtained from the perturbation method of solution of the Boltzmann equation [31] agree with the new results for η . In this case, η is small and constant. This can be observed for relatively large ranges of x_B , in which the perturbation method works (see Fig. 2d).
2. For fast reactions characterized by small ε^* the perturbation method does not work unless some additional conditions for the chemical reaction are fulfilled. This can occur if: (a) an additional quantity (the small steric factor) diminishes the rate of reaction (compare results in Fig. 2a to those in Fig. 2b); (b) the creation of products increases the molar fraction of product x_B , and therefore the rate of the reverse reaction. In this case the apparent (overall) reaction rate decreases, i.e. the reaction becomes

slower. If the molar fraction of product x_B is large enough (see Eq. (30) and Fig. 2a and c) the apparent reaction is slow enough for the perturbation method to work. The effect of nonvanishing products is very important because the value of x_B plays a decisive role in a possibility of use of the result from the perturbation method. For a system without a sufficient amount of products the perturbation method cannot be used because the apparent reaction is too fast. This concerns the system shown in Fig. 2a. For $\varepsilon^* = 1.5$ and x_B large enough, η is equal nearly to 45%.

As discussed by Shizgal and Napier [28], for a very small x_B (x_B nearly equal to 0) the temperature T_B cannot be analyzed because it would become infinite. The breakdown of our inequality (see Eq. (30)), in this extreme limit, is in some way connected with this problem. More generally, the physical meaning of Eq. (30) is that for fast reactions (low values of the right-hand side of Eq. (30)) if x_B is sufficiently small, then this inequality cannot be fulfilled and the perturbation method breaks down.

The results obtained in this Letter are important because they show that the results for η_{CFP} discussed in [21,25] are more general than earlier expected. It means that for the perturbation solution of the Boltzmann equation, the relative change of the rate of chemical reaction does not depend on concentration of reagents. It is interesting that in a somewhat different way Nowakowski [33] has come to the same conclusion. This result is not trivial for us because it confirms the validity of our old analytical results [21,25], which we expected earlier to be valid for so-called quasi stationary state only. Our old η_{CFP} result (see [25]) was first compared for fast reactions with results of Monte Carlo simulations [21] and next (also for slow and very slow reactions) with results from solutions of appropriate differential equations [25] describing the chemically reacting gas. In these researches [21,25] we measured time evolution of T_A . In the range of x_B close to the minimum value of T_A , we obtained nearly constant values of T_A and k_{Af} . We assumed to get ‘a quasi stationary state’ in such a case and we called this minimum a quasi stationary value of

T_A the Shizgal–Karplus temperature. The slower our reaction was, the smaller was x_B for which we got this quasi stationary state. That is why the difference between Eqs. (18) and (21) became very small for very slow reactions, because x_A was nearly equal to 1 for them. However, for fast reactions (for small ε^*) we always had qualitative agreement for η_f as a function of ε^* , since we neglected x_A only. Still, our results were important. They showed the possibility of much larger corrections to the rate of chemical reaction (for small ε^*) than those expected from the earlier treatments [4,6,12]. It should be emphasized that actually, i.e. in this treatment as well as in [31], we use the name Shizgal–Karplus temperature as a description of nonequilibrium temperature in general.

Eqs. (18) and (21) give the same result for $\eta_{Af}(1)$ and $\eta_A(1)$ only in the beginning of a relatively slow reaction. Then the products can be neglected and x_A is nearly equal to 1. This is the fundamental situation for the development of the ideas of Prigogine [1]. It is interesting that Dahler's idea [25] of taking into consideration the reverse reaction in the case of relatively fast chemical reactions (characterized by small ε^*) simplifies the form of the final results. Namely, from the results discussed above it follows that the relative change of the rate of chemical reaction $A + A \rightleftharpoons B + B$ does not depend on the molar fractions of reagents.

Just to summarize, by introducing the non-equilibrium Shizgal–Karplus temperatures (depending on molar fractions of the reagents) into the equilibrium expression for the rate of chemical reaction and by comparing the results obtained with those valid for the equilibrium temperature, we have shown that the relative correction to the rate of chemical reaction does not depend on concentration of reagents. Such a relative correction which had been previously obtained within the perturbation solution of the Boltzmann equation [31] becomes even of about 45%. We have also confirmed the inequalities describing the concentration ranges in which these results are valid. Thus, a completely different procedure to that used in [31] has allowed us to give a sound basis to the claim there stated, of the existence and concen-

tration-independence character of such large effects.

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