

RELATIONS BETWEEN THE ARRHENIUS
ACTIVATION ENERGY AND THRESHOLD ENERGY
FOR SIMPLE MODELS OF THE REACTIVE
CROSS SECTIONS IN A DILUTE GAS

A.S. CUKROWSKI

Institute of Physical Chemistry, Polish Academy of Sciences
Kasprzaka 44/52, 01-224 Warsaw, Poland

and

Faculty of Mathematical and Natural Sciences, Institute of Chemistry
Świętokrzyska Academy, Chęcińska 5, 25-020 Kielce, Poland

cukrowsk@ichf.edu.pl

(Received December 27, 2005; revised version received February 6, 2006)

The Arrhenius activation energy for the reaction $A + A \rightleftharpoons B + B$ in a dilute gas is calculated from a temperature dependence of the rate constant obtained from the perturbation solution of the Boltzmann equation. The first and the second approximation to the velocity distribution function are used in an analysis of nonequilibrium effects. Results obtained for the line-of-centers model and the Prigogine–Xhrouet model of reactive differential cross sections are presented. The Arrhenius activation energy is represented as a function of appropriate threshold energies.

PACS numbers: 05.20.Dd, 82.20.–w, 82.20.Mj, 82.20.Wt

1. Introduction

If a simple chemical reaction is analyzed the activation energy and the threshold energy are often treated as if they were the same quantity. In the kinetic theory of reacting gas this problem can be analyzed if a particular model for the reactive cross section is specified. In this case simple relations between both the quantities can be obtained only if nonequilibrium effects are neglected. Otherwise, such relations have a more complicated form. Prigogine and Xhrouet [1] were the first to show that if a bimolecular chemical reaction proceeds in a dilute gas the Maxwell–Boltzmann velocity distribution function of reacting molecules changes due to nonequilibrium effects. In result the rate constant k_A of chemical reaction decreases. Many authors have analyzed such a decrease and solved the Boltzmann equation for

this purpose (see, *e.g.*, [2] and the references cited therein). Although the line-of-centers model for the reactive cross section (the LC model) has been very often introduced for such a solution it is interesting that even a larger decrease of k_A can be obtained if the model for reactive cross section introduced originally by Prigogine and Xhrouet (the PX model) is used (compare the results from Refs. [3–5]). As the Arrhenius activation energy [6] can be obtained from an analysis of temperature dependence of k_A , it seems interesting to see how, in a case of large nonequilibrium effects, an analysis of such a temperature dependence of k_A can lead to results of the Arrhenius activation energy different from the values of threshold energy. For this purpose it is worthwhile to use the nonequilibrium expressions for k_A obtained for the LC and PX models, *i.e.*, such as obtained in Refs. [3, 5].

The Arrhenius equation can be written in the following form [7]

$$E_{\text{Arr}} = -k \frac{d \ln k_A}{d \frac{1}{T}}, \quad (1.1)$$

where E_{Arr} denotes the Arrhenius activation energy, k is the Boltzmann constant and T the temperature. If in Eq. (1.1) the energy E_{Arr} is expressed for moles of reactants the universal gas constant R instead of k is introduced. It is worthwhile to observe that Arrhenius originally wrote this equation as

$$k_A = A \exp \left(-\frac{E_{\text{Arr}}}{kT} \right), \quad (1.2)$$

where A denotes so called pre-exponential factor. This equation was obtained by Arrhenius [6] after an analysis of earlier experimental data. As this equation is very important in chemical kinetics, many scientists have shown that this equation can be obtained in a theoretical way (see, *e.g.*, [7] and the references cited therein). In general the pre-exponential factor is a function of temperature. The discrepancies from the Arrhenius equation can be analyzed in a relatively simple way on the basis of kinetic theory of gases (see, *e.g.*, [7, 8]). In the simplest case we can analyze the following bimolecular reaction



The rate v_A of this reaction can be written as

$$v_A = v_{\text{Af}} - v_{\text{Ar}} = v_{\text{Af}} - v_{\text{Bf}}, \quad (1.4)$$

where the indices _f and _r are introduced to denote the forward and reverse reactions, respectively, and v_{Ar} is equal to v_{Bf} .

The rates v_{Af} , v_{Bf} , v_A and rate constants k_{Af} , k_{Bf} , k_A are simply related

$$k_{Rf} = \frac{v_{Rf}}{n_R^2}, \quad (R = A, B) \quad (1.5)$$

$$k_A = \frac{v_A}{n_A^2}, \quad (1.6)$$

where n_A is the number density of reactant A .

The rate of the forward chemical reaction can be expressed as

$$v_{Rf} = -\frac{dn_R}{dt} = \iiint f_{R1} f_{R2} \sigma_{re} g d\Omega d\mathbf{c}_{R1} d\mathbf{c}_{R2}, \quad (R = A, B) \quad (1.7)$$

where n_R is the number density, t is the time, f_{R1} and f_{R2} are the velocity distribution functions of two colliding molecules R , distinguished by the indices $R1$ and $R2$, σ_{re} is the differential reactive cross section, Ω is the solid angle, whereas $\mathbf{c}_{R1}$, $\mathbf{c}_{R2}$ and $\mathbf{g}$ are the velocities of molecules and their relative velocity, respectively.

If we neglect the nonequilibrium effects we introduce the Maxwell velocity distribution function

$$f_R^{(0)} = n_R \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left(-\frac{mc_R^2}{2kT} \right), \quad (R = A, B). \quad (1.8)$$

When the reaction (1.3) proceeds the rate of chemical reaction v_A is decreased due to nonequilibrium effects. Prigogine and Xhrouet [1] generalizing the Chapman–Enskog solution [9] of the Boltzmann equation to the case of a chemically reacting gas have shown that the rate constant of the forward reaction k_{Af} is smaller than its equilibrium value $k_{Af}(0)$ because the velocity distribution function is no longer Maxwellian and changes from $f_A^{(0)}$ to f_A . It means that the forward reaction rate changes from $v_{Af}(0)$ to v_{Af} .

If we neglect the nonequilibrium effects we can obtain from Eqs. (1.1) and (1.5)–(1.8) a simplified equilibrium expression for E_{Arr} , however, we have also to choose the appropriate reactive cross section σ_{re} . For the LC model introduced by Present [10] the differential reactive cross section is introduced as

$$\sigma_{re} = \sigma^* = \begin{cases} 0, & g \leq g^*, \\ \frac{1}{4} s_F d^2 (1 - g^{*2}/g^2), & g > g^*, \end{cases} \quad (1.9)$$

where d is the molecular diameter, s_F denotes the steric factor, and g^* is the threshold velocity related to the threshold energy E^* as

$$E^* = \frac{mg^{*2}}{4}. \quad (1.10)$$

As in Ref. [3] we assume that the threshold energies for the forward and reverse reaction are equal, *i.e.*, the reaction is neither exothermal nor endothermal one. In this case for this cross section from Eqs. (1.5), (1.7) and (1.8) we obtain for the forward reaction

$$k_{Rf}^{LC}(0) = 4s_F d^2 \left(\frac{\pi kT}{m} \right)^{1/2} \exp \left(- \frac{E^*}{kT} \right), \quad (R = A, B). \quad (1.11)$$

It should be emphasized that E_{Arr} is a quantity describing the overall reaction. As we are interested in receiving a relation between the Arrhenius activation energy and the threshold energy we analyze the reaction in which the threshold energies for the forward and reverse reactions are equal to one another. This case is very convenient for us because we can use the nonequilibrium expressions for k_A earlier derived [3,5] (see the next section).

After taking into account that if we neglect the nonequilibrium effects we can use for the reaction (1.3) the following relation

$$v_A(0) = v_{Af}(0) \left(1 - \frac{n_B^2}{n_A^2} \right) \quad (1.12)$$

and using Eq. (1.11) for the overall reaction we get

$$k_A^{LC}(0) = 4s_F d^2 \left(\frac{\pi kT}{m} \right)^{1/2} \exp \left(- \frac{E^*}{kT} \right) \left[1 - \frac{n_B^2}{n_A^2} \right]. \quad (1.13)$$

After taking into consideration that in the reaction analyzed the ratio n_B/n_A does not depend on temperature and using Eqs. (1.1) and (1.13) we can get

$$E_{Arr} = E^* + \frac{1}{2} kT. \quad (1.14)$$

This is a known relation which we present only to show the typical way for our further derivations performed in the next section.

For the PX model introduced by Prigogine and Xhrouet [1] the differential reactive cross section is

$$\sigma_{re} = \sigma_0 = \begin{cases} 0, & g \leq g_0, \\ \frac{1}{4} s_F d^2, & g > g_0, \end{cases} \quad (1.15)$$

where g_0 is the appropriate relative threshold velocity related to the threshold energy E_0 as

$$E_0 = \frac{m g_0^2}{4}. \quad (1.16)$$

For the PX model of the differential reactive cross section instead Eqs. (1.11) and (1.13) we can obtain

$$k_{Rf}^{PX}(0) = 4s_F d^2 \left(\frac{\pi kT}{m} \right)^{1/2} \left(\frac{E_0}{kT} + 1 \right) \exp \left(- \frac{E_0}{kT} \right), \quad (R = A, B) \quad (1.17)$$

$$k_A^{PX}(0) = 4s_F d^2 \left(\frac{\pi kT}{m} \right)^{1/2} \left(\frac{E_0}{kT} + 1 \right) \exp \left(- \frac{E_0}{kT} \right) \left[1 - \frac{n_A^2}{n_B^2} \right]. \quad (1.18)$$

From Eqs. (1.1) and (1.18) we get

$$E_{Arr} = E_0 - \frac{1}{2} kT \frac{E_0 - kT}{E_0 + kT}. \quad (1.19)$$

It should be emphasized that this simple relation for the PX model, *i.e.*, Eq. (1.19) in contrary to the relation for the LC model (see Eq. (1.14)) is not generally known. From a comparison of Eqs. (1.14) and (1.19) we see that the relations between the Arrhenius activation energy and the threshold energy are different for the LC and PX models. We have derived Eq. (1.19) here to show that even in the simplest case when the nonequilibrium effects are neglected the role of the model of the reactive cross section is important.

We introduce here the energies in reduced (dimensionless) forms which are convenient to use in more complicated nonequilibrium expressions which we derive in the next section

$$\varepsilon_{Arr} = \frac{E_{Arr}}{kT}, \quad (1.20)$$

$$\varepsilon^* = \frac{E^*}{kT}, \quad (1.21)$$

$$\varepsilon_0 = \frac{E_0}{kT}. \quad (1.22)$$

We will use such energies in the next section. From Eq. (1.14) we can see that if only ε^* is sufficiently large, the threshold energy can be treated as the Arrhenius activation energy, because if ε^* increases the role of $1/2$ becomes smaller and smaller. Relation (1.19) looks even better because, for typical values of ε_0 , *e.g.*, ε_0 ranging from 1 to 50, a role of the term with $1/2$ is diminished. We think that it is important whether the difference between the threshold energy and Arrhenius activation energy can be neglected or not. If only Eqs. (1.14) and (1.19) were sufficient to analyze this problem it would be very simple. However, the nonequilibrium effects can be very important. As we have mentioned the rate constant k_A is diminished because of the

existence of nonequilibrium effects. If the LC model is used the diminishing of k_A due to these effects is not trivial [3] (see also [11, 12]) and for the PX model such effects are even larger [4, 5]. The aim of this paper is to analyze how Eqs. (1.14) and (1.19) are changed if the nonequilibrium effects are taken into account and to see how large the differences between the Arrhenius activation energy and the threshold energy can be in this case. We present such an analysis in the next section.

2. Nonequilibrium expressions for the Arrhenius activation energy for the LC and PX models

In order to take into consideration nonequilibrium effects in expressions relating the Arrhenius activation energy with the threshold energy we use the results obtained from the perturbation solution of the Boltzmann equation. We write down the Boltzmann equation for reaction (see Eq. (1.3)) for the component A in the same form as that presented in Refs. [3, 4, 13].

$$\frac{\partial f_A}{\partial t} = I_{\text{el}} + I_{\text{re}}, \quad (2.1)$$

where the elastic and reactive collision integrals I_{el} and I_{re} are

$$\begin{aligned} I_{\text{el}} = & \int \int (f'_{A1} f'_{A2} - f_{A1} f_{A2}) \sigma_{AA} g d\Omega d\mathbf{c}_{A2} \\ & \times \int \int (f'_A f'_B - f_A f_B) \sigma_{AB} g d\Omega d\mathbf{c}_B, \end{aligned} \quad (2.2)$$

$$I_{\text{re}} = \int \int (f_{B1} f_{B2} - f'_{A1} f'_{A2}) \sigma_{\text{re}} g d\Omega d\mathbf{c}_{B2}, \quad (2.3)$$

where f'_{A1} , f'_{A2} , f'_{B1} , f'_{B2} , f'_A and f'_B are introduced to denote the velocity distribution function after collisions whereas the reactive differential cross sections σ_{re} are those given in Eqs. (1.9) and (1.15) for the LC model and PX model, respectively.

In these integrals the elastic differential cross sections σ_{AA} and σ_{AB} are

$$\sigma_{AA} = \sigma_{AB} = \frac{1}{4} d^2. \quad (2.4)$$

As we have already solved the Boltzmann equation [3, 5] for the LC and PX models of differential reactive cross sections we shall use the results obtained. However, first we shortly describe such results. We have solved the Boltzmann equation by the perturbation method described by Shizgal and Karplus [14, 15] and developed by Shizgal and Napier [2]. We have

neglected all heat effects of the reaction, *i.e.*, we have assumed the reaction to be neither exothermal nor endothermal one. However, we have taken into consideration that, even in the simplest models of reactive collisions, the particles of reactants and products need not have the same average kinetic energies.

Solving the Boltzmann equation (2.1) by the perturbation method we have introduced the nonequilibrium velocity distribution function as

$$f_A = f_A^{(0)} + f_A^{(1)} = f_A^{(0)}(1 + \psi_A) \quad (2.5)$$

and we have expanded the function ψ_A in the Sonine polynomials [9, 15]

$$\psi_A = \sum_i a_A^{(i)} S_{1/2}^{(i)}(\mathcal{C}_A^2), \quad (2.6)$$

where

$$\mathcal{C}_A^2 = \frac{m_A c_A^2}{2kT}. \quad (2.7)$$

It is important to emphasize that the perturbation method can be used only if the quantity ψ_A is small. This is possible in three cases: (*i*) if s_F is small, (*ii*) if the reaction proceeds near to the chemical equilibrium, (*iii*) if the threshold energy, *e.g.*, for the LC model E^* , is significantly larger than kT . Naturally, one or two conditions mentioned above may be sufficient. To make this clear we present the simple expression for ψ_A for the LC model in one Sonine polynomial approximation

$$\psi_A = x_A \left(1 - \frac{x_B^2}{x_A^2}\right) \left[\frac{1}{2} s_F \left(\frac{E^*}{kT} + \frac{1}{2} \right) \exp \left(- \frac{E^*}{kT} \right) \right] S_{1/2}^{(1)}(\mathcal{C}_A^2). \quad (2.8)$$

It is worthwhile to emphasize that, in the chemical equilibrium of the simple reaction (1.3) analyzed in this paper, the molar fractions are equal, *i.e.*, $x_A = x_B = 0.5$.

For the LC and PX models we have used the following three approximations to the velocity distribution function

$$I. \quad f_A(0) = f_A^{(0)}, \quad (2.9)$$

$$II. \quad f_A(1) = f_A^{(0)} [1 + a_A^{(1)}(1) S_{1/2}^{(1)}(\mathcal{C}_A^2)], \quad (2.10)$$

$$III. \quad f_A(2) = f_A^{(0)} [1 + a_A^{(1)}(2) S_{1/2}^{(1)}(\mathcal{C}_A^2) + a_A^{(2)}(2) S_{1/2}^{(2)}(\mathcal{C}_A^2)], \quad (2.11)$$

where the *zero*-th approximation (*I.* — Eq. (2.9)) corresponds to total neglecting of nonequilibrium effects as in the introduction of this paper. In the first approximation (*II.* — Eq. (2.10)) one Sonine polynomial is

introduced only and the coefficient $a_A^{(1)}(1)$ is calculated within the perturbation solution of the Boltzmann equation. In the second approximation (*III.* — Eq. (2.11)) two Sonine polynomials are introduced and two appropriate coefficients $a_A^{(1)}(2)$ and $a_A^{(2)}(2)$ are calculated. In order to derive the expressions for v_A and k_A as a function of the threshold energy we use Eqs. (1.4)–(1.7) and introduce the appropriate velocity distribution function $f_A = f_A(0)$, $f_A = f_A(1)$, $f_A = f_A(2)$. In this way we have got three approximations to v_A for the LC and PX models [3,5]. We have introduced to Eq. (1.7) the velocity distribution functions from Eqs. (2.9)–(2.11) to obtain $v_{Af}(0)$, $v_{Af}(1)$ and $v_{Af}(2)$ and next obtained the expressions for $v_A(0)$, $v_A(1)$ and $v_A(2)$. From those expressions after using Eq. (1.6) and taking into account that for the models analyzed the nonequilibrium corrections to the overall reaction rate v_A do not depend on the concentration of product (see Refs. [3,16]) we can write appropriate simple expressions for the rate constant k_A for the overall reaction.

As follows from results presented in Ref. [3], for the LC model the first and second nonequilibrium approximations for the rate constant for the overall reaction are:

$$k_A^{\text{LC}}(1) = k_A^{\text{LC}}(0) \left[1 - \frac{1}{2} s_F \left(\varepsilon^* + \frac{1}{2} \right) \exp(-\varepsilon^*) \right], \quad (2.12)$$

$$k_A^{\text{LC}}(2) = k_A^{\text{LC}}(0) \left[1 - \frac{1}{2} s_F \left(\varepsilon_1^2 + \frac{1}{30} (\varepsilon_1 - \varepsilon_2)^2 \right) \exp(-\varepsilon^*) \right], \quad (2.13)$$

where $k_A^{\text{LC}}(0)$ is given in Eq. (1.13) and the quantities ε_1 and ε_2 are

$$\varepsilon_1 = \varepsilon^* + \frac{1}{2}, \quad (2.14)$$

$$\varepsilon_2 = \varepsilon^{*2} - \varepsilon^* - \frac{1}{4}, \quad (2.15)$$

where ε^* is the reduced threshold energy defined in Eq. (1.21).

From the results presented in Ref. [5] it follows that for the PX model the corresponding first and second nonequilibrium approximations for the rate constant of the overall reaction are

$$k_A^{\text{PX}}(1) = k_A^{\text{PX}}(0) \left[1 - \frac{1}{2} s_F \frac{e_1^2}{\varepsilon_0 + 1} \exp(-\varepsilon_0) \right], \quad (2.16)$$

$$k_A^{\text{PX}}(2) = k_A^{\text{PX}}(0) \left[1 - \frac{1}{60} s_F \left(\frac{e_1 e_3 + e_2 e_4}{\varepsilon_0 + 1} \right) \exp(-\varepsilon_0) \right], \quad (2.17)$$

where the quantities e_1 , e_2 , e_3 , and e_4 are

$$e_1 = \varepsilon_0^2 + \frac{1}{2}\varepsilon_0 + \frac{1}{2}, \quad (2.18)$$

$$e_2 = -\varepsilon_0^3 + 2\varepsilon_0^2 + \frac{1}{4}\varepsilon_0 + \frac{1}{4}, \quad (2.19)$$

$$e_3 = -\varepsilon_0^3 + 33\varepsilon_0^2 + \frac{63}{4}\varepsilon_0 + \frac{63}{4}, \quad (2.20)$$

$$e_4 = -\varepsilon_0^3 + 3\varepsilon_0^2 + \frac{3}{4}\varepsilon_0 + \frac{3}{4}. \quad (2.21)$$

In order to get an expression for the Arrhenius activation energy as a function of the threshold energy we can use Eqs. (1.1) and (1.20) and introduce an appropriate equation for k_A . For the LC model after such an introduction of k_A from Eqs. (1.13), (2.12) and (2.13) we get

$$\varepsilon_{\text{Arr}}^{\text{LC}}(0) = \varepsilon^* + \frac{1}{2}, \quad (2.22)$$

$$\varepsilon_{\text{Arr}}^{\text{LC}}(1) = \frac{L(1)}{C(1)}, \quad (2.23)$$

where

$$L(1) = (2\varepsilon^* + 1) [8 \exp(\varepsilon^*) - (8\varepsilon^{*2} - 2\varepsilon^* + 1)s_{\text{F}}], \quad (2.24)$$

$$C(1) = 2 [8 \exp(\varepsilon^*) - (2\varepsilon^* + 1)^2 s_{\text{F}}], \quad (2.25)$$

$$\varepsilon_{\text{Arr}}^{\text{LC}}(2) = \frac{L(2)}{C(2)}, \quad (2.26)$$

where

$$L(2) = 960(2\varepsilon^* + 1) \exp(\varepsilon^*) - (64\varepsilon^{*5} - 368\varepsilon^{*4} + 2400\varepsilon^{*3} + 552\varepsilon^{*2} - 12\varepsilon^* + 129) s_{\text{F}}, \quad (2.27)$$

$$C(2) = 1920 \exp(\varepsilon^*) - (32\varepsilon^{*4} - 128\varepsilon^{*3} + 1040\varepsilon^{*2} + 1056\varepsilon^* + 258) s_{\text{F}}. \quad (2.28)$$

For the PX model using Eqs. (1.18), (2.16) and (2.17) in the same way as that described above for the LC model we obtain

$$\varepsilon_{\text{Arr}}^{\text{PX}}(0) = \varepsilon_0 - \frac{1}{2} \frac{(\varepsilon_0 - 1)}{(\varepsilon_0 + 1)}, \quad (2.29)$$

$$\varepsilon_{\text{Arr}}^{\text{PX}}(1) = \frac{P(1)}{X(1)}, \quad (2.30)$$

where

$$P(1) = (2\varepsilon_0^2 + \varepsilon_0 + 1) [8 \exp(\varepsilon_0) - (8\varepsilon_0^3 - 10\varepsilon_0^2 + \varepsilon_0 + 1)s_F] , \quad (2.31)$$

$$X(1) = 2 [8(\varepsilon_0 + 1) \exp(\varepsilon_0) - (2\varepsilon_0^2 + \varepsilon_0 + 1)s_F] , \quad (2.32)$$

$$\varepsilon_{\text{Arr}}^{\text{PX}}(2) = \frac{P(2)}{X(2)} , \quad (2.33)$$

where

$$P(2) = 960(2\varepsilon_0^2 + \varepsilon_0 + 1) \exp(\varepsilon_0) - (64\varepsilon_0^7 - 560\varepsilon_0^6 + 3264\varepsilon_0^5 - 2088\varepsilon_0^4 + 84\varepsilon_0^3 - 1011\varepsilon_0^2 + 258\varepsilon_0 + 129)s_F , \quad (2.34)$$

$$X(2) = 2[960(\varepsilon_0 + 1) \exp(\varepsilon_0) - (16\varepsilon_0^6 - 96\varepsilon_0^5 + 600\varepsilon_0^4 + 528\varepsilon_0^3 - 681\varepsilon_0^2 + 258\varepsilon_0 + 129)s_F] . \quad (2.35)$$

Fig. 1. represents the ratio of the Arrhenius activation energy and the threshold energy calculated for the LC model from Eqs. (2.22)–(2.28) and represented as a function of the reduced threshold energy ε^* . Such a ratio for the PX model calculated from Eqs. (2.29)–(2.35) and represented as a function of ε_0 is given in Fig. 2.

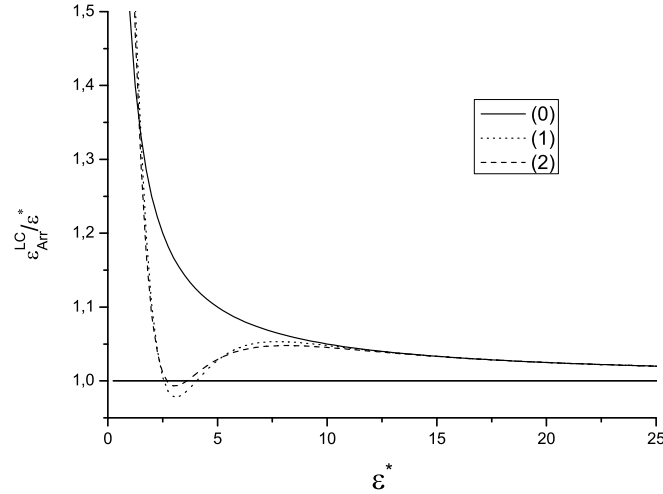


Fig.1. The ratio $\varepsilon_{\text{Arr}}^{\text{LC}}/\varepsilon^*$ as a function of ε^* for the equilibrium results — (0) and those using one — (1) and two — (2) nonequilibrium corrections to the rate constant for the LC model.

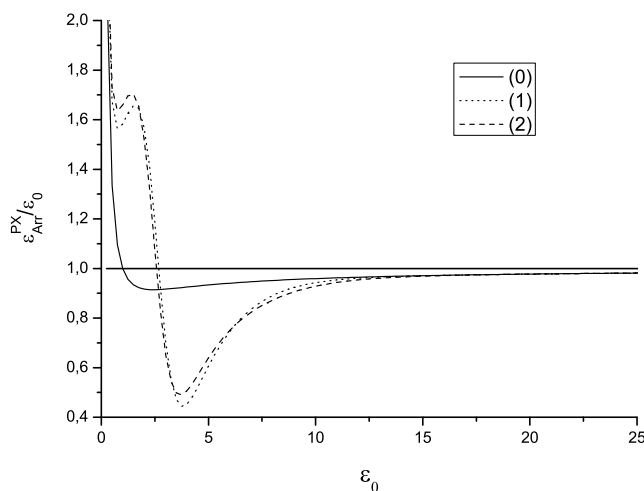


Fig. 2. The ratio $\varepsilon_{\text{Arr}}^{\text{PX}}/\varepsilon_0$ as a function of ε_0 for the PX model presented in the same way as in Fig. 1.

3. Discussion

We have derived equations relating the Arrhenius activation energy to the threshold energy. First, we have written down such equations for the simplest case of the Maxwellian velocity distribution function for molecules, *i.e.*, for Eq. (1.8) which is used in the equilibrium. Next, after taking into account the nonequilibrium effects, for the line-of-centers model, the simple equilibrium relation (2.22) changes to Eqs. (2.23), (2.26) corresponding to the first and second approximations to the velocity distribution function (obtained from the perturbation solution of the Boltzmann equation), respectively. For the Prigogine–Xhrouet model such an equilibrium relation (see Eq. (2.29)) changes to Eqs. (2.30), (2.33) for such nonequilibrium approximations. As we can see, for both the models analyzed, the differences between the Arrhenius activation energy and the threshold energy can be practically neglected if only those energies are large enough. Even the role of the nonequilibrium effects diminishing the values of the rate constant of chemical reaction is not important in this case. However, the situation becomes completely different if the Arrhenius activation energy is small. We know that for very small values of ε_{Arr} the problem of choosing of the appropriate model can be important, and for some models of reactive cross sections not only small but even negative ε_{Arr} can appear [7, 17–19]. For small positive values of ε_{Arr} , *e.g.*, ranging from 1 to 8 the difference following from introduction of the LC or PX model can be important. In these ranges of ε_{Arr} if only the non-equilibrium effects are neglected the differences between $\varepsilon_{\text{Arr}}^{\text{PX}}$ and ε_0 calculated for the PX model are even smaller

than such differences between $\varepsilon_{\text{Arr}}^{\text{LC}}$ and ε^* for the LC model (see Fig. 1. and Fig. 2.). But if these nonequilibrium effects are taken into consideration, as the nonequilibrium corrections to the rate constant are more pronounced for the PX model than for the LC model, such nonequilibrium corrections to the Arrhenius activation energy are also more pronounced for the PX model.

Just to summarize, we have shown for both the models that the Arrhenius activation energy can be changed due to the nonequilibrium effects. Such corrections are larger for the Prigogine–Xhrouet model than for the line-of-centers model if the appropriate threshold energy is small.

The author would like to thank the Polish State Committee for Scientific Research (KBN) for the financial support. Additionally, the author would like to thank also his son M. Sc. M.J. Cukrowski Jr. from Warsaw University of Technology, Faculty of Mathematics and Information Science for a help in some final computer evaluations and editorial preparations of the paper.

REFERENCES

- [1] I. Prigogine, E. Xhrouet, *Physica* **15**, 913 (1949).
- [2] B.D. Shizgal, D. Napier, *Physica* **A223**, 50 (1996).
- [3] A.S. Cukrowski, *Physica* **A275**, 134 (2000).
- [4] A.S. Cukrowski, S. Fritzsche, M.J. Cukrowski Jr., *Chem. Phys. Lett.* **379**, 193 (2003).
- [5] A.S. Cukrowski, S. Fritzsche, *Acta Phys. Pol. B* **34**, 3607 (2003).
- [6] S. Arrhenius, *Z. Phys. Chem.* **4**, 226 (1889).
- [7] W. Stiller, *Arrhenius Equation and Non-Equilibrium Thermodynamics*, Teubner Texte Phys., B 21, Leipzig 1989.
- [8] H. Eyring, S.H. Lin, S.M. Lin, *Basic Chemical Kinetics*, Wiley, New York 1980.
- [9] S. Chapman, T.G. Cowling, *The Mathematical Theory of Nonuniform Gases*, Cambridge Univ. Press, Cambridge 1970.
- [10] R.D. Present, *J. Chem. Phys.* **31**, 747 (1959).
- [11] A.S. Cukrowski, J. Popielawski, Lihong Qin, J.S. Dahler, *J. Chem. Phys.* **97**, 9086 (1992).
- [12] J. Gorecki, B.Ch. Eu, *J. Chem. Phys.* **97**, 6695 (1992).
- [13] A.S. Cukrowski, S. Fritzsche, J. Fort, *Chem. Phys. Lett.* **341**, 585 (2001).
- [14] B. Shizgal, M. Karplus, *J. Chem. Phys.* **52**, 4262 (1970).
- [15] B. Shizgal, M. Karplus, *J. Chem. Phys.* **54**, 4345 (1971).
- [16] B. Nowakowski, *J. Chem. Phys.* **109**, 3443 (1998).
- [17] A.S. Cukrowski, W. Stiller, R. Schmidt, *Theor. Chim. Acta* **73**, 67 (1988).
- [18] W. Stiller, R. Schmidt, E. Mueller, N.V. Shokheriev, *Z. Phys. Chem. Neue Folge* **162**, 119 (1989).
- [19] A.S. Cukrowski, M.A. Telka, *Chem. Phys. Lett.* **279**, 402 (1998).