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Kinetic description of bimolecular reactions with low energy cross sections in dilute gases

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The rate v of bimolecular chemical reaction $A+A=B+C$ is analyzed for simple models of reactive cross sections. Collisions of particles colliding with energy E larger than a relatively low characteristic energy E_L are either non-reactive (reversed Prigogine-Xhrouet model = rPX) or the ability to react is decreasing for $E > E_L$ (reversed line-of-centres model = rLC). After solution of the Boltzmann equation analytical expressions for the distribution function f and the rate coefficient k have been derived. It is shown that the Arrhenius activation energy E_A is small and even negative for sufficiently small E_L. The non-equilibrium corrections to v are small.

Key words: Activation energy — Boltzmann equation — Cross section — Gases — Reaction kinetics

1. Introductory remarks and definitions

As follows from the kinetic theory [1, 2] a chemical reaction in dilute gas can be analyzed on the basis of Boltzmann equation [3]. Such an analysis is the simplest if the reaction is analyzed in such a stage that the products may be neglected [3-5]. The neglection of products has been thoroughly analyzed by Pyun and Ross [6]. This neglection has been introduced in many other papers [7-18] because it permits to simplify the description of various non-equilibrium phenomena in a chemically reacting gas. The equilibrium description of the rate coefficient for numerous models of reactive cross sections was presented, e.g. by Menziger and Wolfgang [19], Le Roy [20], and Stiller and Naumann [21].

For the simplest chemical reaction

$$A+A\rightarrow B+C \tag{1}$$

for which the products B and C can be neglected the Boltzmann equation can be written with standard notation in the following form [1, 11]

$$\frac{\partial f}{\partial t}=\iint (f'f'_1-ff_1)\sigma_{\mathrm{el}}(g,\Omega)g\,d\Omega\,dc_1 - \iint ff_1\sigma_{\mathrm{re}}(g,\Omega)g\,d\Omega\,dc_1, \tag{2}$$

where f and f' denote the molecular velocity distribution function of component A before and after collision, respectively, t is the time, $\sigma_{\mathrm{el}}(g,\Omega)$ and $\sigma_{\mathrm{re}}(g,\Omega)$ are the differential elastic and reactive cross sections, respectively. The solid angle Ω specifies the orientation of the relative velocity vector after collision

$$\boldsymbol{g}'=\boldsymbol{c}'_1-\boldsymbol{c}' \tag{3}$$

to the initial relative velocity

$$\boldsymbol{g}=\boldsymbol{c}_1-\boldsymbol{c}. \tag{4}$$

The rate v of chemical reaction is

$$v=-\frac{dn}{dt}=kn^2=\iiint ff_1\sigma_{\mathrm{re}}(g,\Omega)g\,d\Omega\,dc_1\,dc, \tag{5}$$

where n is the number density of component A and k denotes the rate coefficient of chemical reaction

$$k=(1/n^2)\iiint ff_1\sigma_{\mathrm{re}}(g,\Omega)g\,d\Omega\,dc_1\,dc. \tag{6}$$

In the case of generalization of hard spheres model the differential elastic and reactive cross sections may be expressed by probabilities $\alpha_{\mathrm{el}}(g)$ and $\alpha_{\mathrm{re}}(g)$ of elastic and reactive collisions, respectively and by the diameter of hard sphere in the following way

$$\sigma_{\mathrm{el}}(g)=\int_{4\pi}\sigma_{\mathrm{el}}(g,\Omega)\,d\Omega=\alpha_{\mathrm{el}}(g)\pi d^2 \tag{7}$$

$$\sigma_{\mathrm{re}}(g)=\int_{4\pi}\sigma_{\mathrm{re}}(g,\Omega)\,d\Omega=\alpha_{\mathrm{re}}(g)\pi d^2, \tag{8}$$

where $\sigma_{\mathrm{el}}(g)$ and $\sigma_{\mathrm{re}}(g)$ are the total elastic and reactive cross sections, respectively, whereas

$$\alpha_{\mathrm{el}}(g)+\alpha_{\mathrm{re}}(g)=1. \tag{9}$$

The probability $\alpha_{\mathrm{re}}(g)$ can be represented as a function of relative kinetic energy of approaching particles

$$E=(m/4)g^2, \tag{10}$$

where m is the mass of the particle and additionally as a function of the steric factor s_F connected with an orientation of particles during the collisions.

Usually the dependence of the reactive cross section on energy can be represented in the following simplified way [3, 5]: It is zero for energies smaller than a threshold energy E_0 (the barrier of the reaction) and greater than zero for higher energies. According to Eq. (8) the reactive cross section is simply related to the probability of reactive collisions. Such probabilities for the models used in [3, 5] are shown in Fig. 1. The maximum value of the probability for these models equals 1 although in more general case it can be equal to $s_F \leq 1$. Such cross sections are limited with the idea that there must be a minimum relative kinetic energy of the particles in order to react. In the region $E < E_0$ only elastic collisions occur. Many gas reactions between molecules or molecules and radicals can be approximately described by such and similar simple cross sections [21].

It is known, however, that e.g. combination or recombinations of radicals or some molecule reactions can occur mainly for low energies E. For such reactions several authors (see, e.g. [9, 10, 13, 22–26]) performed their calculations of the rate coefficient of chemical reaction both in equilibrium and in reaction-induced non-equilibrium situations. Latter point can be important for reactions with low threshold energy $E_0 \ll k_B T$, where k_B is the Boltzmann constant and T denotes temperature. Because for such reactions E_0 does not appear in a formula for reactive cross section this may make an impression that the threshold energy is negligibly small and therefore also the activation energy can be neglected. That is why such reactions were treated as reactions without activation energy [9, 11]. Although for the line-of-centres model [5] in the description of chemical reaction with the use of the equilibrium velocity distribution functions for the large Arrhenius activation energies E_A the quantities E_0 and E_A are nearly the same [19–21, 27] it seems to be doubtful if neglection of E_0 in a formula for reactive cross section is in general case equivalent with $E_A = 0$.

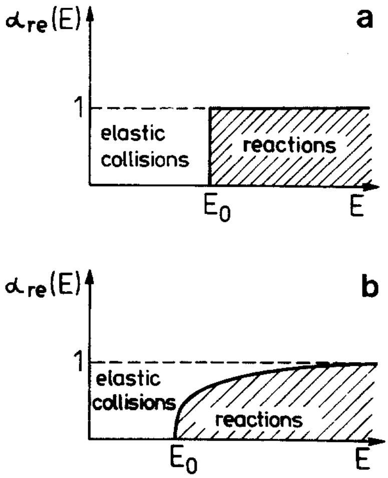

Fig. 1. "High-energy" cross sections $\sigma_{\mathrm{re}} = \pi d^2 \alpha_{\mathrm{re}}(E)$ for translationally driven reactions. **a** σ_{PX} (Prigogine-Xhrouet model [1]); **b** σ_{LC} (line-of-centres model [2])

In this paper we intend to analyze more carefully equilibrium and non-equilibrium description of reactions which proceed in a low energy region of cross sections. Namely, we want to describe such reactions which can occur for low energies, but will be stopped or gradually diminished for energies higher than a relatively low characteristic energy E_L. Such reactions present in a sense the reverse situation to those of Fig. 1. In order to study such low energy reactions we intend to use the simple models of reactive cross sections. According to Eq. (8) for the situations described above we can introduce two models: (1) The reversed Prigogine-Xhrouet model (shortly denoted by indices rPX), and (2) the reversed line-of-centres model (denoted by indices rLC) in the following way

$$\alpha_{\mathrm{rPX}}(g)=\begin{cases}1-\alpha_{\mathrm{PX}}(g)=1 & E\le E_L\\ 1-\alpha_{\mathrm{PX}}(g)=0 & E>E_L\end{cases} \tag{11}$$

$$\alpha_{\mathrm{rLC}}(g)=\begin{cases}1-\alpha_{\mathrm{LC}}(g)=1 & E\le E_L\\ 1-\alpha_{\mathrm{LC}}(g)=E_L/E=g_L^2/g^2 & E>E_L,\end{cases} \tag{12}$$

where $\alpha_{\mathrm{PX}}(g)$ and $\alpha_{\mathrm{LC}}(g)$ are the probabilities of reactive collisions for Prigogine-Xhrouet model and line-of-centre model, respectively, and g_L is the value of g corresponding to $E=E_L$ (see Eq. (10)). After introduction of the steric factor the total reactive cross section for these models are

$$\sigma_{\mathrm{rPX}}(g)=\begin{cases}s_F\pi d^2=\pi d_{\mathrm{re}}^2 & E\le E_L\\ 0 & E>E_L\end{cases} \tag{13}$$

$$\sigma_{\mathrm{rLC}}(g)=\begin{cases}s_F\pi d^2=\pi d_{\mathrm{re}}^2 & E\le E_L\\ s_F\pi d^2 g_L^2/g^2=\pi d_{\mathrm{re}}^2 g_L^2/g^2=\pi d_{\mathrm{re}}^2 E_L/E & E>E_L,\end{cases} \tag{14}$$

where d_{re} is the diameter of the reactant simply connected with the diameter of hard sphere d and the steric factor s_F

$$d_{\mathrm{re}}^2=s_F d^2. \tag{15}$$

The latter models are shown in Fig. 2. A comparison of Fig. 2 with Fig. 1 makes possible to see all the differences between the models discussed. In order to make

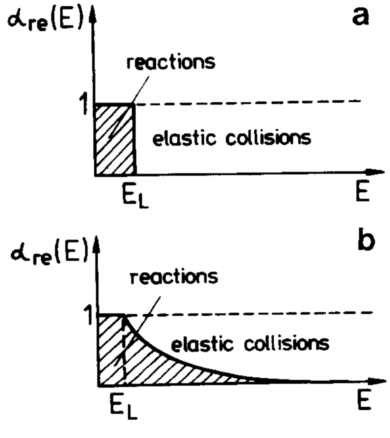

Fig. 2. "Low-energy" cross sections $\sigma_{\mathrm{re}}=\pi d^2\alpha_{\mathrm{re}}(E)$ for **a** σ_{rPX} (reversed Prigogine-Xhrouet model); **b** σ_{rLC} (reversed line-of-centres model)

this comparison transparent we have introduced in Figs. 1 and 2 and in Eqs. (11) and (12) $s_F = 1$ although in general $s_F \leq 1$.

The aim of this paper is to analyze the low energy models introduced in Eqs. (11)-(15) and shown in Fig. 2, i.e. the rPX- and rLC-models. We shall perform this analysis in order to derive the expressions for the rate coefficients k of chemical reactions. After using of Present's solution [5] of the Boltzmann equation (in Sect. 2) we shall first analyze (in Sect. 3) $k^{(0)}$ obtained with the equilibrium velocity distribution functions and then, (in Sect. 4) $k^{(1)}$ is obtained with the non-equilibrium velocity distribution functions. The analysis of $k^{(0)}$ will enable us to see the relations between the Arrhenius activation energy and E_L, whereas from the analysis of $k^{(1)}$ we shall evaluate the non-equilibrium corrections to the rate coefficients. Some final remarks will be given in the discussion (Sect. 5).

2. The solution of the Boltzmann equation

In order to get the solution we follow the way chosen by Present [5]. We write the velocity distribution function as

$$f = f^{(0)} + f^{(1)} = f^{(0)}(1+\phi), \tag{16}$$

where $f^{(0)}$ is the Maxwell-Boltzmann equilibrium velocity distribution function

$$f^{(0)} = n(m/2\pi k_B T)^{3/2} \exp(-mc^2/2k_B T), \tag{17}$$

whereas $f^{(1)}$ is the first non-equilibrium correction to $f^{(0)}$. We use the result of Sonine polynomials expansion of ϕ from [3, 5] which can be written as

$$\phi = a_2 S^{(2)}_{1/2}(\mathscr{C}^2) \tag{18}$$

where

$$\mathscr{C}^2 = mc^2/2k_B T \tag{19}$$

$$S^{(2)}_{1/2} = 15/8 - (5/2)\mathscr{C}^2 + (1/2)\mathscr{C}^4. \tag{20}$$

As follows from [3, 5] we can calculate a_2 from the equation

$$a_2 = \alpha_2 / a_{22}, \tag{21}$$

where

$$a_{22} = 4n^2 d^2 (\pi k_B T/m)^{1/2} \tag{22}$$

and

$$\alpha_2 = -(\pi^2/64)(m/\pi k_B T)^{3/2}[15K_3 - 5(m/k_B T)K_5 - (1/4)(m/k_B T)^2 K_7], \tag{23}$$

where

$$K_n = \int_0^\infty \exp(-mg^2/4k_B T)\alpha_{\mathrm{re}}(g) g^n \, dg. \tag{24}$$

Similarly to Eq. (16) for f we can write the rate v of chemical reaction and its rate coefficient k as follows [28]

$$v = v^{(0)} + v^{(1)} \tag{25}$$

$$k = k^{(0)} + k^{(1)}, \tag{26}$$

where as shown already by Present [5]

$$\begin{aligned} v^{(0)} = n^2 k^{(0)} &= \int\!\!\int\!\!\int f^{(0)} f_1^{(0)} \sigma_{\mathrm{re}}(g, \Omega) g \, d\Omega \, dc_1 \, dc \\ &= (1/2)\pi^2 n^2 d^2 (m/\pi k_B T)^{3/2} K_3 \end{aligned} \tag{27}$$

and

$$\begin{aligned} v^{(1)} = n^2 k^{(1)} &= -2a_2\alpha_2 \\ &= -v^{(0)}[(4k_B T/m)^2 a_2^2/K_3]. \end{aligned} \tag{28}$$

From the equations presented in this section and the definitions for the models discussed in the previous section it is possible to perform all necessary calculations.

3. The rate of chemical reaction calculated for equilibrium velocity distribution function – relations between Arrhenius activation energy and the energy E_L

In order to derive the expressions for $v^{(0)}$ and $k^{(0)}$ we use Eqs. (27) and (24) for the models defined in Eqs. (11)-(15). According to the explanation given in the description of Figs. 1 and 2 we introduce in Eq. (24) for the rPX-model and the rLC-model

$$\alpha_{\mathrm{re}}(g) = s_F \alpha(g). \tag{29}$$

In order to make the descriptions shorter we introduce the reduced energies ε as

$$\varepsilon = E/k_B T. \tag{30}$$

After performing necessary integrations we get

$$v_{\mathrm{rPX}}^{(0)} = k_{\mathrm{rPX}}^{(0)} n^2 = 4\pi d_{\mathrm{re}}^2 n^2 (\pi k_B T/m)^{1/2} [1 - (1 + \varepsilon_L) \exp(-\varepsilon_L)] \tag{31}$$

$$v_{\mathrm{rLC}}^{(0)} = k_{\mathrm{rLC}}^{(0)} n^2 = 4\pi d_{\mathrm{re}}^2 n^2 (\pi k_B T/m)^{1/2} [1 - \exp(-\varepsilon_L)]. \tag{32}$$

It is worthwhile to observe that the fraction of reactive collisions F_{re} is

$$\begin{gathered} F_{\mathrm{re}} = v^{(0)} / \lim_{\varepsilon_L \to \infty} v^{(0)} \\ s_F = 1. \end{gathered} \tag{33}$$

From Eqs. (30)-(33) and (15) it follows that

$$F_{\mathrm{re}}^{\mathrm{rPX}} = s_F [1 - (1 + \varepsilon_L) \exp(-\varepsilon_L)] \tag{34}$$

$$F_{\mathrm{re}}^{\mathrm{rLC}} = s_F [1 - \exp(-\varepsilon_L)]. \tag{35}$$

The quantities $F_{\mathrm{re}}^{\mathrm{rPX}}$ and $F_{\mathrm{re}}^{\mathrm{rLC}}$ may be useful in discussion of non-equilibrium effects.

The Arrhenius activation energy E_A is defined by equation

$$k = A_0 \exp(-E_A/k_B T) = A_0 \exp(-\varepsilon_A), \tag{36}$$

where A_0 is the so-called preexponential factor. From this definition it follows that

$$E_A = k_B T^2 \, d \ln k/dT. \tag{37}$$

From Eqs. (37), (31) and (15) after assuming that the steric factor does not depend on temperature we obtain

$$\varepsilon_A^{\mathrm{rPA}} = \frac{1}{2} + \frac{\varepsilon_L^2}{1 + \varepsilon_L - \exp \varepsilon_L}, \tag{38}$$

whereas from Eqs. (37) and (32) in the same way we get

$$\varepsilon_A^{\mathrm{rLC}} = \frac{1}{2} + \frac{\varepsilon_L}{1 - \exp \varepsilon_L}. \tag{39}$$

Similar relations between the Arrhenius activation energy and the threshold energy E_0 has been already derived for various "high-energy" cross sections models by Menziger and Wolfgang [19], Le Roy [20] and Stiller [29]. From Eqs. (38) and (39) it can be easily seen that

$$\lim_{\varepsilon_L \to 0} \varepsilon_A^{\mathrm{rPX}} = -\tfrac{3}{2} \tag{40}$$

$$\lim_{\varepsilon_L \to 0} \varepsilon_A^{\mathrm{rLC}} = -\tfrac{1}{2}. \tag{41}$$

It means that for these models if the characteristic energy E_L is sufficiently low the Arrhenius activation energy can be negative. The conditions for the negativity of E_A are:

$$\frac{\varepsilon_L^2 \exp(-\varepsilon_L)}{1 - (1 + \varepsilon_L) \exp(-\varepsilon_L)} > \frac{1}{2} \quad (\mathrm{rPX}) \tag{42}$$

$$\frac{\varepsilon_L \exp(-\varepsilon_L)}{1 - \exp(-\varepsilon_L)} > \frac{1}{2} \quad (\mathrm{rLC}). \tag{43}$$

These results are reasonable because for the models discussed in this paper the rate coefficient of chemical reaction should decrease with the increase of the temperature, contrary to the rate coefficient of many chemical reactions in which only the collisions of molecules possessing relative velocities large enough are reactive.

From Eqs. (38) and (39) it can be also seen that

$$\lim_{\varepsilon_L \to \infty} \varepsilon_A^{\mathrm{rPX}} = \lim_{\varepsilon_L \to \infty} \varepsilon_A^{\mathrm{rLC}} = \tfrac{1}{2}. \tag{44}$$

This result has no physical value unless the steric factor is not small enough. From comparison of Eqs. (40), (41), and (44) it follows that the Arrhenius

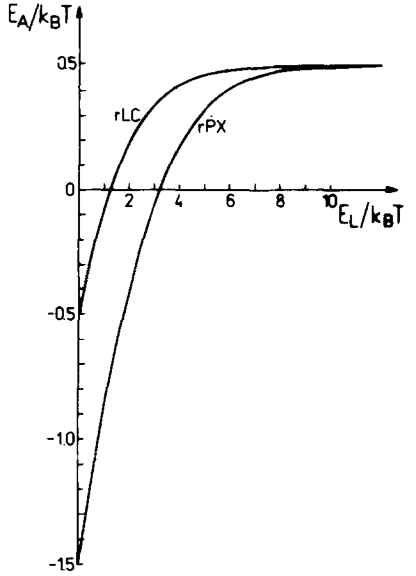

Fig. 3. Reduced activation energy $\varepsilon_A = E_A/k_BT$ versus the reduced low characteristic energy $\varepsilon_L = E_L/k_BT$ for the rPX- and rLC-models

activation energies E_A^{rPX} and E_A^{rLC} increase with the increase of E_L. Fig. 3 gives the numerical results for E_A/k_BT against E_L/k_BT for the both models. The resulting ranges of negative activation energies are: in the rPX-model for $E_L^{\mathrm{rPX}}/k_BT < 3.215$ (i.e. for $E_L^{\mathrm{rPX}} < 8.0$ kJ/mole at 300 K) and in the rLC-model for $E_L^{\mathrm{rLC}}/k_BT < 1.255$ (i.e. for $E_L^{\mathrm{rLC}} < 3.1$ kJ/mole at 300 K).

In such an analysis it is also convenient to write down Eqs. (38) and (39) in the following way

$$E_A^{\mathrm{rPX}}/E_L = \frac{1}{2\varepsilon_L} + \frac{\varepsilon_L}{1 + \varepsilon_L - \exp \varepsilon_L} \tag{45}$$

$$E_A^{\mathrm{rLC}}/E_L = \frac{1}{2\varepsilon_L} + \frac{1}{1 - \exp \varepsilon_L}. \tag{46}$$

Fig. 4 shows E_A/E_L against k_BT/E_L in the rLC-model. The ratio E_A^{rLC}/E_L is negative for temperatures T greater than 401 K, 600 K, and 802 K if E_L is 1 kJ/mole, 1.5 kJ/mole, and 2 kJ/mole, respectively. Similar tendencies can be

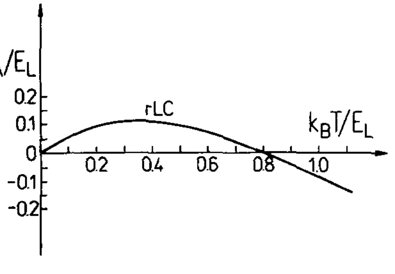

Fig. 4. Ratio E_A/E_L versus k_BT/E_L for the rLC-model

found for the rPX model: E_A^{rPX}/E_L is negative for $k_BT/E_L > 0.312$, i.e. the energy E_L must be less than 8 kJ/mole at 300 K and less than 10.7 kJ/mole at 400 K.

4. Non-equilibrium corrections to the rate of chemical reaction

The relative correction to the rate of chemical reaction can be written as

$$\eta = -(v - v^{(0)})/v^{(0)} = -v^{(1)}/v^{(0)} = -k^{(1)}/k^{(0)}. \tag{47}$$

We shall present here the results for η for the models discussed, as well as the expressions for a_2 (see Eqs. (18) and (21)) because this quantity permits to see how much the velocity distribution function is changed in connection with chemical reaction. From Eqs. (21)-(24) and Eqs. (29), (30), (11), (12) it follows

$$a_2^{\mathrm{rPX}} = (-s_F/32)\{-1+[1+\varepsilon_L+8\varepsilon_L^2-4\varepsilon_L^3]\exp(-\varepsilon_L)\} \tag{48}$$

and

$$a_2^{\mathrm{rLC}} = (-s_F/32)\{-[1-\exp(-\varepsilon_L)]+4\varepsilon_L(1-\varepsilon_L)\exp(-\varepsilon_L)\}. \tag{49}$$

From Eqs. (47), (28), (24) and Eqs. (29), (30), (11), (12) we get the relative corrections to the rate of chemical reaction in the following forms

$$\eta^{\mathrm{rPX}} = \frac{s_F\{-1+[1+\varepsilon_L+8\varepsilon_L^2-4\varepsilon_L^3]\exp(-\varepsilon_L)\}^2}{512[1-(1+\varepsilon_L)\exp(-\varepsilon_L)]} \tag{50}$$

$$\eta^{\mathrm{rLC}} = \frac{s_F\{-[1-\exp(-\varepsilon_L)]+4\varepsilon_L(1-\varepsilon_L)\exp(-\varepsilon_L)\}^2}{512[1-\exp(-\varepsilon_L)]}. \tag{51}$$

From Eqs. (50) and (51) it follows that

$$\lim_{\varepsilon_L\to 0} \eta^{\mathrm{rPX}} = \lim_{\varepsilon_L\to 0} \eta^{\mathrm{rLC}} = 0 \tag{52}$$

$$\lim_{\varepsilon_L\to \infty} \eta^{\mathrm{rPX}} = \lim_{\varepsilon_L\to \infty} \eta^{\mathrm{rLC}} = \lim_{\varepsilon_0\to 0} \eta^{\mathrm{LC}} = s_F/512, \tag{53}$$

where η^{LC} denotes η for the line-of-centres model. In Fig. 5 we present the fractions of reactive collisions F_{re} (calculated from Eqs. (34) and (35)) and the quantities a_2 (calculated from Eqs. (48) and (49)) as functions of E_L/k_BT. We present these quantities as $F_{\mathrm{re}}^{\mathrm{rPX}}/s_F$, $F_{\mathrm{re}}^{\mathrm{rLC}}/s_F$, a_2^{rPX}/s_F and a_2^{rLC}/s_F, respectively. Fig. 6 shows the relative corrections η to the rate of chemical reaction as functions of E_L/k_BT. We present these quantities as η^{rPX}/s_F and η^{rLC}/k_BT, respectively.

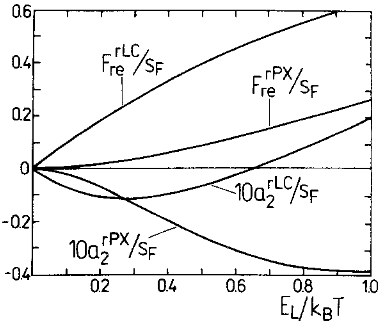

Fig. 5. The quantities a_2 and F_{re} (defined in the Eqs. (18) and (33), respectively) divided by the steric factor s_F as functions of $\varepsilon_L = E_L/k_BT$

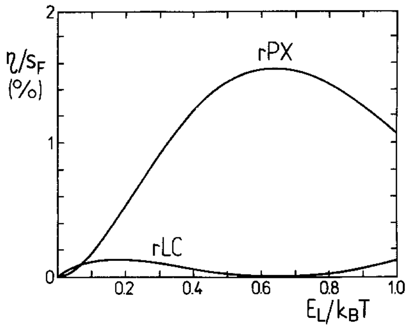

Fig. 6. Relative non-equilibrium corrections η to the rate coefficient (divided by the steric factor s_F) versus $\varepsilon_L = E_L/k_BT$

5. Discussion

From Eqs. (31) and (32) describing the equilibrium rates $v^{(0)}$ and rate coefficients $k^{(0)}$ it can be seen that for the both models discussed the typical weakly temperature dependent factor $4\pi d_{\mathrm{re}}^2 n^2(\pi k_B T/m)^{1/2}$ (corresponding to the collision frequency [1]) and steric factor appears. This factor is exactly the same as the preexponential factor in the line-of-centres model [5]. The remaining factor $[1-\cdots]$ deviates in a characteristic manner from the exponential term of "high-energy" reactions.

The relations between the Arrhenius activation energy E_A and the energy E_L can be seen from Eqs. (38)-(44) and Figs. 3 and 4. For E_L approaching to zero the minimum values of E_A for rPX and rLC-models are $E_A^{\mathrm{rPX}} = -1.5k_BT$ and $E_A^{\mathrm{rLC}} = -0.5k_BT$, respectively. For the both models E_A is an increasing function of E_L. For greater energies E_L the transition from a "low-energy"- to a "high-energy"-reaction is performed with $E_A = 0.5k_BT$ for $E_L \to \infty$. Naturally the last result has not physical value but it shows the tendency. The value of $E_A = 0$ is obtained in the rPX-model for $E_L^{\mathrm{rPX}} \approx 3.21k_BT$ and in rLC-model for $E_L^{\mathrm{rLC}} \approx 1.25k_BT$. Although such values of E_L are not very low, such and even greater values of E_L can be used in the models discussed if the steric factor s_F is sufficiently small. As it can be seen from Eqs. (45), (46) and Fig. 4 the values of E_A and E_L can differ considerably.

The interesting phenomenon of occurence of the negative Arrhenius activation energies E_A for the both low-energy models can be explained with equations derived by Tolman [30]. According to Tolman the quantity E_A can be described as follows

$$E_A = \langle E_R \rangle - (3/2)RT, \tag{54}$$

where R is the universal gas constant and

$$\langle E_R \rangle = \frac{\int_0^\infty dE\, E^2 \sigma_R(E) \exp(-E/RT)}{\int_0^\infty dE\, E \sigma_R(E) \exp(-E/RT)}. \tag{55}$$

The first term $\langle E_R \rangle$ gives the average molar energy of chemically "successful", i.e. reactive collisions, whereas the second term contains the average kinetic energy $N_A(3/2)k_BT$ of a mole of the gas (N_A-Avogadro's number). For "high-energy" reactions the nominator is obtained over integration of the integrand $E^2\sigma_R E \exp(-E/RT)$ from a threshold energy E_0 to infinity leading in general to positive activation energies, because $\langle E_R \rangle > N_A(3/2)k_BT$.

In our case of "reversed" cross sections σ_R, which are not equal to zero only in the low-energy region, the integrand is - at least for small E_L - considerably reduced leading only to a non-vanishing contribution to $\langle E_R \rangle$ for the interval $0 \leq E \leq E_L$. Therefore for small E_L situations can occur in which $\langle E_R \rangle < N_A(3/2)k_BT$ leading to negative Arrhenius activation energies.

It is interesting that in the limiting case of $E_L \rightarrow 0$ for the rPX-model the first right-hand term in Eq. (54), i.e. $\langle E_R \rangle$ would be equal to zero, whereas for the rLC-model $\langle E_R \rangle = N_Ak_BT$ (see Eqs. (40) and (41)). We would like to emphasize here that the chemical reactions described by the simple models discussed should not be treated as "reactions without activation energy" but as "reactions with small activation energy" or even as "reactions with small negative activation energy".

From the further analysis performed in Sect. 4 it follows that the value of quantities a_2 characterizing the non-equilibrium corrections to the velocity distribution function (see Eqs. (16)-(18)) are smaller than the values of F_{re} defined in Eq. (33) as fraction of reactive collisions (compare Eqs. (48) and (49) to Eqs. (34) and (35) and see also Fig. 5). It means that even for relatively large F_{re}, say $F_{\mathrm{re}} = 0.1$ the value of a_2 is small. We make the comparisons for $s_F = 1$; e.g. for the rPX-model for $\varepsilon_L^{\mathrm{rPX}} = 0.5$ we get $F_{\mathrm{re}}^{\mathrm{rPX}} = 0.09$ and $a_2^{\mathrm{rPX}} = -0.025$, whereas for the rLC-model for $\varepsilon_L^{\mathrm{rLC}} = 0.1$ we get $F_{\mathrm{re}}^{\mathrm{rLC}} = 0.095$ and $a_2^{\mathrm{rLC}} = -0.0072$. It is interesting that in the limiting case of $E_L \rightarrow \infty$ the values of a_2 are $a_2^{\mathrm{rPX}} = a_2^{\mathrm{rLC}} = -s_F/32$. It is worthwhile to emphasize that the effect of corrections of a_2 on the velocity distribution function is even smaller because of existence of the Sonine polynomial $S_{1/2}^2(\mathscr{C}^2)$ (see Eqs. (16), (18)-(20)), e.g. as follows from Eq. (20) for the typical value $\mathscr{C} = 1$ we get $S_{1/2}^2(1) = -\frac{1}{8}$. That is why the results for relative correction η to the rate of chemical reaction are so small for the models discussed (see Eqs. (50), (51) and Figs. 5 and 6). This shows the same tendency which could be seen from the models discussed in [8, 9, 11, 26].

We would like to point out that in the models used in our paper always is $E_A^{\mathrm{rLC}} > E_A^{\mathrm{rPX}}$ for all finite E_L. For greater E_L the "low-energy" concept remains valid if the steric factor s_F is small enough.

It is interesting that in these models in the limiting case of $E_L \rightarrow \infty$ corresponding to $E_0 \rightarrow 0$ for the line-of-centres model [5] exactly the same results for η are obtained (see Eq. (53)). The same result for η was discussed by Pyun (see Eq. (13) in [10]).

Just to summarize, using very simple models we have shown that (i) in some reactions with low-energy cross sections the Arrhenius activation energy can be very small and even be negative, (ii) the non-equilibrium corrections to the rate of chemical reaction are very small similarly to those obtained for so-called "models with zero activation energy".

For concrete reactions the cross sections have to be chosen more sophisticated. It is possible, too, to extend these calculations to more complex situations (several components with reaction partners of different masses).

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