Vol. 28 (1997) *ACTA PHYSICA POLONICA B* No 8

ON THE INFLUENCE OF NONEQUILIBRIUM EFFECTS ON A THERMALLY ACTIVATED CHEMICAL REACTION *

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(Received January 14, 1997)

The influence of nonequilibrium effects on the rate constant of a thermally activated reaction $A + A \to$ products is investigated. The considered model for molecules of both reactant and products takes into account the energy transfer from the internal degrees of freedom to those relevant for reaction. The results of molecular dynamics simulations performed within a model of reactive hard spheres are compared with a simple phenomenology based on the assumption on the Maxwellian form of reactant's energy distribution. A good agreement between both methods was obtained.

PACS numbers: 05.70. Ln, 82.20. Wt, 82.20. Mj

1. Introduction

Nonequilibrium effects which may arise in systems with thermally activated chemical reactions have been intensively studied for more then 50 years [1, 2]. They appear because the reaction cross section for a thermally activated process depends on energy of interacting molecules of reactants. The probability of reaction is large for molecules with high energy, whereas there are no reactive collisions if the energy is low. As the result, the most energetic molecules of reactant are transformed into a product and a nonequilibrium

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* Presented at the IX Symposium on Statistical Physics, Zakopane, Poland, September 23–28, 1996.

contribution to the energy distribution appears. The average quantities, like for example the rate constant or the diffusion constant, calculated on the basis of the nonequilibrium energy distribution are different then those characterising the equilibrium system [3–5]. Most of the studies on this subject were based on the Boltzmann equation [2, 4, 5] and the molecules of reactants were modelled as structureless spheres. The recent microscopic simulations of nonequilibrium effects in systems with a thermally activated chemical reaction, performed using molecular dynamics [6] and the Bird simulation technique [4], have shown that an accurate description of these effects may be obtained if one assumes that the energy distribution of reactant's molecules retains Maxwellian form, but the temperature it corresponds to, is different than the temperature of the system as a whole. The concept, that many "temperatures" may characterise a system simultaneously is widely used in spectroscopy, where different "temperatures" are used to describe translational, rotational or vibrational energy distribution of a molecule.

In this paper we study the nonequilibrium effects associated with the reaction:

$$A + A \rightarrow \text{products}(B + C)\ ,$$

Contrary to the previous works on this subject the molecules of both reactant an product have internal degrees of freedom. Therefore the system is characterised by four different energy distributions simultaneously. One can easily give a simple phenomenological description of the nonequilibrium effects by assuming, like it was done in [6], the Maxwellian form for the energy distribution of the reactant. The comparison with results of molecular dynamics simulation shows that such approximation describes system's evolution with a good accuracy.

2. Molecular dynamics simulations

In our molecular dynamics simulations we use sphere-in- sphere model in order to describe a molecule with internal degrees of freedom. The molecules of the system considered are represented by spheres with a spherical cavity inside. There is another small sphere in this cavity. The large sphere moves freely in the whole space and collides with the other large ones. Its kinetic energy represents the energy related to the degrees of freedom which are important for a chemical reaction. The motion of a smaller sphere is of course restricted to the cavity and the small sphere can collide with the big sphere surrounding it only. It is assumed that collisions between big and small spheres are elastic. The kinetic energy of a small sphere represents the energy of the internal degrees of freedom, which do not influence reaction cross section directly. In this model the energy at equilibrium is equally divided between "chemical" and " internal" degrees of freedom and in average it is equal to $3/2k_BT$. This value does not depend on sphere masses or diameters.

The frequency of collisions between a big sphere and a small sphere trapped inside it determines the rate of energy transfer between "chemical" and "internal" degrees of freedom. It depends on all parameters describing the spheres. In our simulations we assumed that the masses of both big and small sphere are equal. The cavity is homocentratic with the centre of a big sphere. Its radius is equal to this of the big sphere. Therefore, in our model if the diameters of a big sphere and of small sphere are fixed than the density of big spheres (*i.e.* the packing fraction) is the only parameter, which controls the ratio of collision frequencies between big and big and between big and small spheres.

The described model may be easily modified in order to increase the number of internal degrees of freedom by introducing more then one object moving in the cavity. If the internal degrees of freedom are represented by the kinetic energy of hard objects than the energy transfer between chemical and internal degrees of freedom occurs in collisions only. A potential-based interaction between small and big spheres would lead to continuos energy transfer between these degrees of freedom . However, from the numerical point of view it is more convenient to study and record system's evolution using a single algorithm for the nearest collision, rather then to mix methods for hard sphere evolution of the large spheres with a step-by-step solution for motion of a trapped object in a potential field.

In order to describe a reactive collision we adopt the line-of-centre [7] model for a thermally activated reaction. Let the activation energy for a considered process equals E_A. A collision between big spheres is regarded as reactive if in the centre of masses reference system (for big spheres only) the kinetic energy associated with the motion of big spheres along the line of their centres exceeds E_A. Let us notice that the existence of small spheres has no influence on reaction because the probability of an instantaneous collision of three hard spheres is null. In simulations presented below we assume that the heat of studied reaction is equal to zero.

In order to make computer simulations efficient we used the technique described in [4] and [8]. First we calculate the evolution without reactions and store the trajectory. Next having recorded information on a equilibrium trajectory we can easily obtain the evolution of a system with reactions. It is just necessary to choose the time reaction starts, mark all the spheres as reactants, read the information about consecutive collisions and check if they lead to reaction or not. Simulations give information on concentrations of reagents and on the properties of energy distribution for reactant and product as functions of time (the procedure was described in [8]).

The results present below were obtained for $n_0 = 512$ big spheres all with same diameter $d_C = 5$, which represented "chemical" properties of molecules. A small spheres with diameter $d_I = 2.5$ is moving inside each big sphere. The masses of both big and small sphere are equal to $32 a.u.$ The ratio of frequency of collisions between big spheres and between big and the corresponding small sphere is controlled by system's packing fraction. We have considered three different packing factors $\eta = 0.155, 0.238, 0.398$. The results for the average energies related to different degrees of freedom and for the rate constant for activation energies $E_A = 2$, and $3k_BT$ are shown in Figs. 1–5.

3. Phenomenological description of nonequilibrium effects

The simplest theoretical approach, which describes nonequilibrium effects in systems with a thermally activated reaction, is based on the assumption that if at the beginning the energy distribution for molecules of reactant is the equilibrium one than it retains Maxwellian form for all the time reaction proceed. Of course, during the evolution the temperature of the system as a whole becomes different than the time dependent "temperature" of reactant. Here we adopt this method for the system with internal degrees of freedom. Let us assume that energy distribution of both internal and chemical degrees of freedom for particles of reactant A has the Maxwellian form corresponding to time dependent temperatures $T_{I,A}(t), T_{C,A}(t)$ respectively. Moreover, it is assumed that the internal and chemical degrees of freedom are uncorrelated so at each moment of time, the probability density $f_A(\bar{v}_C, \bar{v}_I, t)$ of finding a particle of A with the velocities $\bar{v}_C, \bar{v}_I$, for the outer and the inner spheres respectively, factories as follows:

$$f_A(\bar{v}_C, \bar{v}_I, t) = f_{T_{C,A}(t)}(\bar{v}_C) \cdot f_{T_{I,A}(t)}(\bar{v}_I) , \tag{1}$$

where $f_{T_{C,A}(t)}(\bar{v}_C)$ and $f_{T_{I,A}(t)}(\bar{v}_I)$ are the Maxwellians corresponding to $T_{I,A}(t)$ and $T_{C,A}(t)$ respectively. Now one may easily derive the equations, which describe the time evolution of concentration of A and the density of energy for molecules of A and of products. The reaction cross section for the line of centre model reads [7]:

$$\sigma_{A,A} = \begin{cases} \frac{1}{4} s_F d_C^2 \left(1 - \frac{E_A}{E_C}\right) & \text{for } E_C \geq E_A \\ 0 & \text{for } E_C < E_A \end{cases} . \tag{2}$$

In this formula s_F stands for the steric factor and

$$E_C = m \frac{(\bar{v}_1 - \bar{v}_2)^2}{4} , \tag{3}$$

where $\bar{v}_1$ and $\bar{v}_2$ denote precollision velocities of colliding spheres.For the line-of-centre model the equation describing the time evolution for concentration of A reads [9]:

$$\frac{da}{dt} = -k\left(T_{C,A}(t)\right) a^2 \, , \tag{4}$$

where

$$k\left(T_{C.A}(t)\right) = s_F 4 d_C^2 g_{AA} \left(\frac{\pi k_B T_{C,A}(t)}{m}\right)^{1/2} \exp\left(-\frac{E_A}{k_B T_{C,A}(t)}\right) , \tag{5}$$

and g_{AA} is the value of the radial distribution function of big spheres at the distance equal to their diameter.

The equations describing time evolution of the density of energy for the internal and chemical degrees of freedom can be obtained if one consider the chemical reaction and the energy transfer [9]. The internal energy of molecules of A decreases because after a reactive collision the energy of inner spheres becomes the internal energy for a molecule of product. The collisions between the outer and the inner spheres contribute to the exchange of energy between the internal and chemical degrees of freedom. Taking these two processes into account one obtains the following equation:

$$\begin{aligned} \frac{d}{dt}\left(\frac{3}{2} k_B a T_{I,A}(t)\right) &= 4 {d^*}^2 g^* \left(\frac{\pi k_B (T_{I,A} + T_{C,A})}{2m}\right)^{1/2} k_B (T_{C,A} - T_{I,A}) a \\ &- s_F 4 d^2 g_{AA} \left(\frac{\pi k_B T_{C,A}}{m}\right)^{1/2} \exp\left(-\frac{E_A}{k_B T_{C,A}}\right) \frac{3}{2} k_B T_{I,A} a^2 \, , \end{aligned} \tag{6}$$

where $d^* = (d_C - d_I)/2$ and g^* denotes the geometric factor, which contributes to the frequency of collisions between the inner and the outer spheres, in the same way as the radial distribution function does for the collision between big spheres. The equation describing the time evolution for the density of energy of the chemical degrees of freedom of reactant can be obtained in the similar way when one considers the chemical reaction and two possible ways of energy exchange: in collisions between the outer and the inner spheres in particles representing A as described before and in collisions between particles representing A and those representing products. The equation has the form:

$$\begin{aligned} \frac{d}{dt}\left(\frac{3}{2} k_B a T_{C,A}(t)\right) &= 4 {d^*}^2 g^* \left(\frac{\pi k_B (T_{I,A} + T_{C,A})}{2m}\right)^{1/2} k_B (T_{I,A} - T_{C,A}) a \\ &- s_F 4 d_C^2 g_{AA} \left(\frac{\pi k_B T_{C,A}}{m}\right)^{1/2} \exp\left(-\frac{E_A}{k_B T_{C,A}}\right) \frac{3}{2} k_B T_{C,A} a^2 \left(\frac{7}{4} + \frac{E_A}{2 k_B T_{C,A}}\right) \\ &+ 4 d_C^2 g_{AA} \left(\frac{\pi k_B (T_0 + T_{C,A})}{2m}\right)^{1/2} k_b (T_0 - T_{C,A}) a n_0 \, . \end{aligned} \tag{7}$$

By introducing the scaled variables:

— time in units describing the frequency of collisions between big spheres

$$\tau = 4d^2 g_{AA} \left(\frac{\pi k_B T_0}{m} \right)^{1/2} n_0^2 t \,,$$

— concentration in units corresponding to the total density:

$$\alpha = \frac{a}{n_0} \,,$$

— temperatures scaled to the temperature of the system as a whole

$$\xi_I = \frac{T_{I,A}}{T_0} \qquad \xi_C = \frac{T_{C,A}}{T_0} \,,$$

and the activation energy:

$$\varepsilon_A = \frac{E_A}{k_B T_0} \,,$$

one obtains the following evolution equations:

$$\frac{d}{d\tau}\alpha = -\xi_C^{1/2} \exp\left(-\frac{\varepsilon_A}{\xi_C} \right) \alpha^2 \,, \tag{8}$$

$$\frac{d}{d\tau}\xi_I = \frac{2}{3} c_f \left(\frac{\xi_C + \xi_I}{2} \right)^{1/2} (\xi_C - \xi_I) \,, \tag{9}$$

$$\begin{aligned} \frac{d}{d\tau}\xi_C = & -\xi_C^{1/2} s_F \exp\left(-\frac{\varepsilon_A}{\xi_C} \right) \frac{1}{3} \left(\frac{\xi_C}{2} + \varepsilon_A \right) \alpha \\ & + \frac{2}{3} \left(\frac{1}{2} + \frac{\xi_C}{2} \right)^{1/2} (1 - \xi_C) + \frac{2}{3} c_f \left(\frac{1}{2}(\xi_I + \xi_c) \right)^{1/2} (\xi_I - \xi_c) \,, \end{aligned} \tag{10}$$

where c_F is the ratio of the frequency of collision between inner and outer spheres and the frequency of collisions between the large spheres. For any initial condition Eqs. (7)–(9) can be easily solved numerically. If ξ_I and ξ_C are known than the concentration of products (b) and the energy densities: internal $E_{I,B}$ and chemical $E_{C,B}$ can be calculated from:

$$b = n_0(1 - \alpha) \,, \tag{11}$$

$$E_{I,B} = \frac{3}{2} k_B T_0 \frac{1 - \alpha\xi_I}{1 - \alpha} \,, \tag{12}$$

$$E_{C,B} = \frac{3}{2} k_B T_0 \frac{1 - \alpha\xi_C}{1 - \alpha} \,, \tag{13}$$

Moreover, the rate constant at time t can be calculated from Eq. (5). The results obtained by numerical solution of Eqs. (8)–(13) are plotted in Figs. 1–5 using a solid line. In the limiting case of very low rate of energy transfer between internal and chemical degrees of freedom it is expected that the energy accumulated in internal degrees of freedom has no influence on systems evolution. Putting $c_f = 0$ one obtains

$$\frac{d}{d\tau}\alpha = -\xi_C^{1/2} s_F \exp\left(-\frac{\varepsilon_A}{\xi_C}\right)\alpha^2 , \tag{14}$$

$$\begin{aligned}\frac{d}{d\tau}\xi_C &= -\xi_C^{1/2} s_F \exp\left(-\frac{\varepsilon_A}{\xi_C}\right)\frac{1}{3}\left(\frac{\xi_C}{2}+\varepsilon_A\right)\alpha \\ &+\frac{2}{3}\left(\frac{1}{2}+\frac{\xi_C}{2}\right)^{1/2}(1-\xi_C) ,\end{aligned} \tag{15}$$

and such set of equations describes nonequilibrium effects in a system structureless spheres [6]. For comparison we plot a numerical solution of Eqs. (14), (15) in Figs. 1, 2 and 5 using the dashed line.

Let us notice that Eq. (10) may be rewritten as

$$\begin{aligned}\frac{d}{d\tau}\xi_C + \frac{d}{d\tau}\xi_I = &-\xi_C^{1/2} s_F \exp\left(-\frac{\varepsilon_A}{\xi_C}\right)\frac{1}{3}\left(\frac{\xi_C}{2}+\varepsilon_A\right)\alpha \\ &+\frac{2}{3}\left(\frac{1}{2}+\frac{\xi_C}{2}\right)^{1/2}(1-\xi_C) ,\end{aligned} \tag{16}$$

In the case when the energy transfer between the internal and chemical degrees of freedom is very effective ($c_f \to \infty$) Eq. (9) gives $\xi_I = \xi_C$. Now from Eq. (16) it follows that:

$$\begin{aligned}\frac{d}{d\tau}\xi_C &= -\frac{1}{2}\Bigg\{\xi_C^{1/2} s_F \exp\left(-\frac{\varepsilon_A}{\xi_C}\right)\frac{1}{3}\left(\frac{\xi_C}{2}+\varepsilon_A\right)\alpha \\ &+\frac{2}{3}\left(\frac{1}{2}+\frac{\xi_C}{2}\right)^{1/2}(1-\xi_C)\Bigg\} .\end{aligned} \tag{17}$$

As expected the decrease in reactant's energy is equally shared between chemical and internal degrees of freedom. The results of Table I compare the minimum value of the rate constant (scaled to the equilibrium value of rate constant) and the concentrations of reactant for which the maximum nonequilibrium effects is expected obtained for low rate of energy transfer (Eqs(14), (15)) with these for high energy transfer (Eqs. (14), (17)) and with the results for a hypotetic system with 4 internal degrees of freedom and infinitely fast energy transfer (thus 1/5 stands instead of 1/2 in Eq. (17)). Steric factor is taken as equal to 1. It comes out that the strength of nonequilibrium effect is not significantly changed by the presence of the internal degrees of freedom. On the other hand, the range of concentrations, in which the nonequilibrium effect is the most important is shifted towards higher concentrations of product if the number of internal degrees of freedom is increasing.

TABLE I

The maximum nonequilibrium effect on the rate constant as a function of the activation energy and the rate of energy transfer. The minimum of scaled rate constant is given together with the concentration of products it corresponds to. In calculations $s_F = 1$, the cases I, II and III correspond to very low energy transfer, very high energy transfer for sphere-in-sphere case and to very high energy transfer in a system with 4 internal degrees of freedom, respectively.

ε_A	I	II	III
0.5	0.875 (0.53)	0.904 (0.65)	0.938 (0.78)
1	0.810 (0.43)	0.846 (0.56)	0.893 (0.71)
1.5	0.776 (0.34)	0.809 (0.46)	0.859 (0.63)
2	0.768 (0.26)	0.796 (0.38)	0.841 (0.54)
2.5	0.779 (0.20)	0.800 (0.30)	0.837 (0.46)
3	0.802 (0.15)	0.816 (0.23)	0.844 (0.37)

4. Results and discussion

Figures 1–5 show the comparison between results of molecular dynamics simulations (points) and phenomenology (the solid line) for a few selected systems. For all reactions considered $s_F = 1$. The average energy corresponding to the chemical degrees of freedom of reactant, scaled to the value of thermal energy for an average particle of the whole system is shown in Fig. 1. The system is characterised by packing fraction $\eta = 0.393$ and for this density $c_f = 0.7$. The activation energy for the reaction considered is $\varepsilon_A = 2$. The time evolution of ξ_C is very similar to the evolution of "temperature" of reactant in a system without internal degrees of freedom (for comparison we plot it using a dashed line). At the beginning ξ_C decreases because the most energetic particles of A are transformed into product. At a certain concentration of reactant the energy exchange with molecules of product starts to dominate over the energy decrease related to reaction and ξ_C increases to its equilibrium value. The maximum nonequilibrium effects corresponds to the minimum in ξ_C. As expected (Table I) for system with internal degrees of freedom the decrease in ξ_C is less pronounced than for structureless particles and it is shifted towards larger concentrations of products.

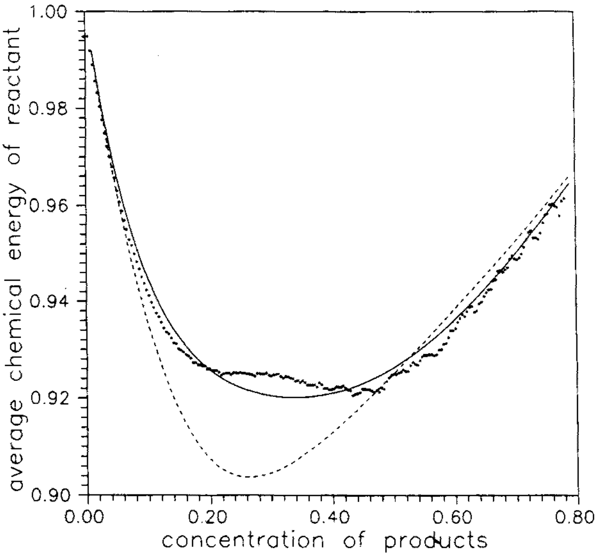

Fig. 1. The average energy for the chemical degrees of freedom of reactant, scaled to $3/2k_BT_0$, as a function of concentration of products. The solid line shows phenomenological result (Eqs. (8), (10)) and points represented molecular dynamics data. For comparison we give the time evolution of the average energy of reactant in the case of structureless molecules (Eqs. (14), (15)) (the dashed line).

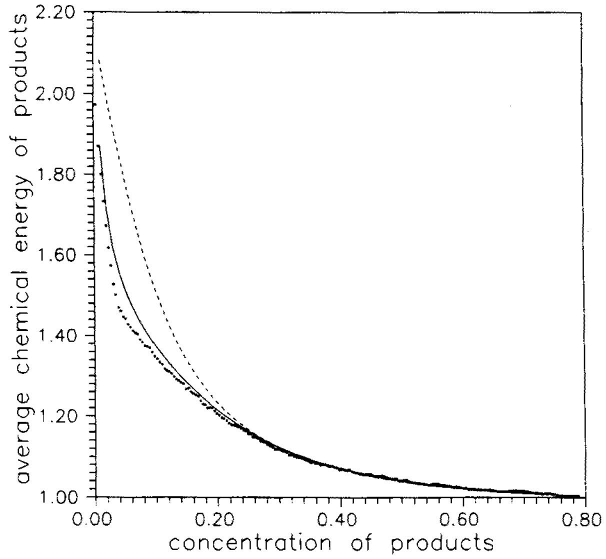

Fig. 2. The average energy for the chemical degrees of freedom for products, scaled to $3/2k_BT_0$, as a function of concentration of products. Notation as in Fig. 1.

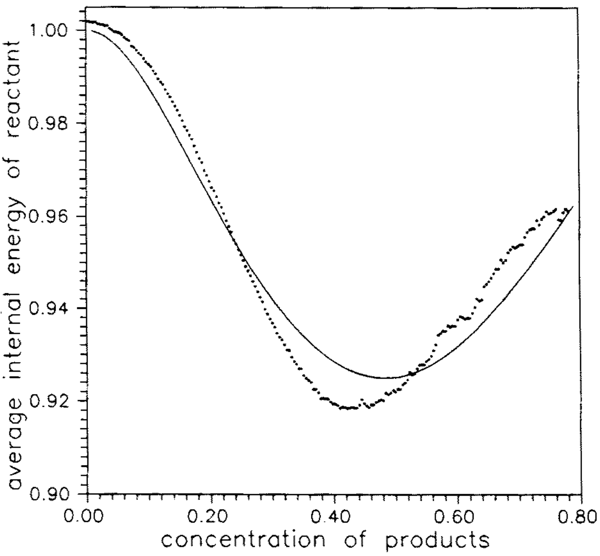

Fig. 3. The average energy for the internal degrees of freedom for reactant A, scaled to $3/2k_BT_0$, as a function of concentration of products. The solid line shows phenomenological result (Eqs. (8)–(10)) and points represent molecular dynamics data.

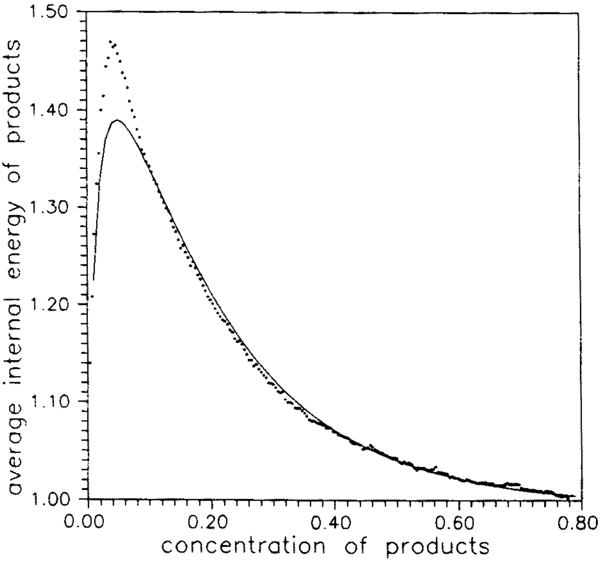

Fig. 4. The average energy for the internal degrees of freedom for products, scaled to $3/2k_BT_0$, as a function of concentration of products. Notation as in Fig. 3.

The time evolution of the average energy associated with the chemical degrees of freedom of product (Fig. 2) is also very similar to the results obtained for the average energy of product in a system without internal degree of freedom. Like in the later case this energy is monotonically decreasing function of concentration. The results shown in Fig. 2 were obtained for $\eta = 0.155(c_f = 4.08)$ and $\varepsilon_A = 3$. For comparison the average energy of products in a system without the internal degree of freedom is shown (the dashed line).

The evolution of the average energy associated with internal degrees of freedom for reactant is shown in Fig. 3. If the transfer rate of energy between chemical and internal degrees of freedom of A is very fast then $\xi_I(t)$ is almost the same as $\xi_C(t)$: The results presented in Fig. 3 were calculated for $\eta = 0.393$ and therefore the energy transfer mentioned above is quite slow $(c_f = 0.7)$. At the beginning the energy related to internal degrees of freedom of A remains close to the equilibrium value. The maximum decrease in internal energy of A occurs for much larger concentration of B than it is for the chemical energy of A (compare with Fig. 1).

Fig. 4 shows the most interesting time evolution of the average energy associated with the internal degrees of freedom for product. At the beginning it is equal to the equilibrium temperature of the system as a whole. As reactions start the energy is transferred from the chemical to internal degrees of freedom of product and the average energy reaches its maximum. Finally it decreases due to the energy transfer from products to the reactant. The results presented in Fig. 4 were obtained for $\eta = 0.155$.

It is worthwhile to notice that for the time evolution of the average energies the agreement between molecular dynamics simulation and phenomenology is very good. The theory, which takes the internal degrees of freedom into account gives much better description of the nonequilibrium effects than the phenomenology for structureless particles.

Figs. 5a and 5b show the rate constants for the processes characterised by activation energies $\varepsilon_A = 2$ and $\varepsilon_A = 3$ respectively. Simulation were performed for $\eta = 0.238$, which corresponds to $c_f = 1.983$. Large dispersion of molecular dynamic results (points) is related to the limited size of recorded trajectory (750000 collisions were recorded). The rate constant calculated on the basis of phenomenology (Eq. (5)) predicts slightly larger nonequilibrium effects than observed in simulations. The agreement between theory and simulations improves at higher activation energies. We believe that the discrepancies between phenomenology and simulations observed at low activation energies are related to correlations between the energies of the outer and the inner spheres. Our theory neglects these correlations completely (Eq. (1)) whereas in simulations we observed an increased (by about 30 %)

that a hot small sphere moves inside a highly energetic large one. We believe that, in despite of its simplicity, the phenomenology based on the concept of different temperatures which characterise various degrees of freedom of molecules may be useful for an approximate description of nonequilibrium effects in chemical systems.

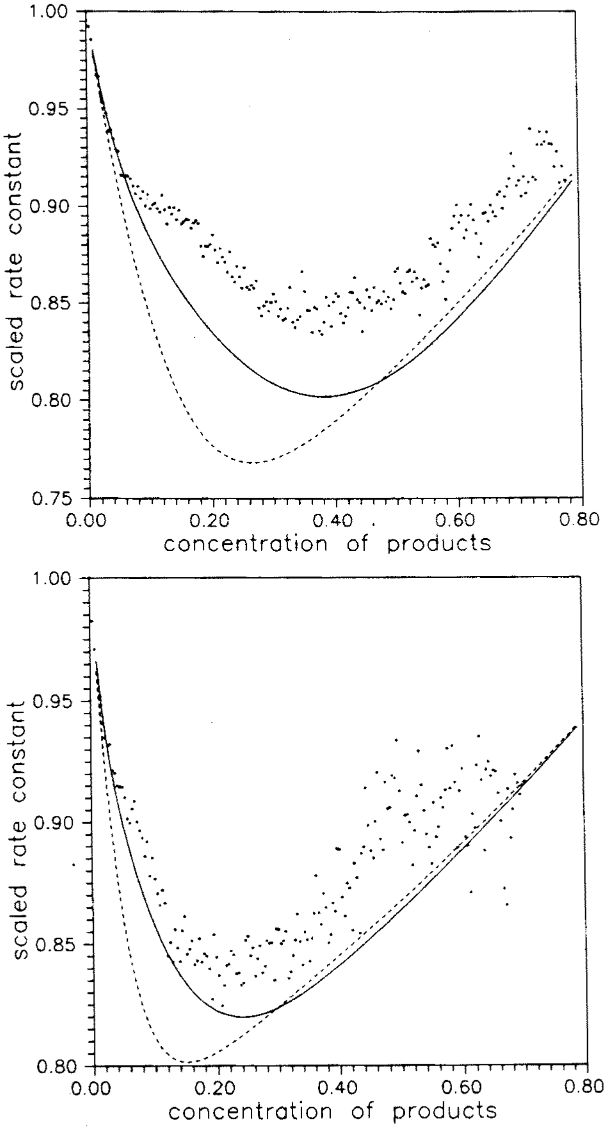

Fig. 5. The rate constant scaled to the equilibrium value as a function of concentration of products. Notation as in Fig. 1. The phenomenological rate constant was calculated using Eq. (5). (a) — $\varepsilon_A = 2$; (b) — $\varepsilon_A = 3$.

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