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On the Stochastic Theory of Adiabatic Thermal Explosion in Small Systems—Numerical Results

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The stochastic methods are applied for a description of adiabatic thermal explosion. The master equation is solved numerically for the system of 1000 molecules. The inverse reaction is neglected in our basic model, but we also study the case when this reaction is taken into account. For both models two maxima of probability distribution are observed for a certain period of time. It is shown that for low initial temperature the adiabatic thermal explosion is a process of high dispersion and the phenomenological description of this reaction can fail.

KEY WORDS: Fluctuations; master equation; adiabatic thermal explosion.

1. INTRODUCTION

It is known that combustion(1) is one of many chemical processes that display far-from-equilibrium behavior like periodicity and chaotic evolution. In this paper we study the adiabatic thermal explosion, where observed nonequilibrium effects are connected with great changes of temperature during the reaction. The adiabatic thermal explosion, together with the chemical explosion,(7) are relatively simple reactions where far-from-equilibrium evolution is prominent. In these cases the coupling between the dynamics of chemical process and fluctuations in the system can be so strong that fluctuations are self-accelerated. The dispersion of such processes can be very high and it can cause transient bimodality. The phenomenological description of chemical reaction deals with the average density of molecules. Such information is of small value when the dispersion of process is high. Therefore, the stochastic methods must be applied

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because they give the time evolution of the density of probability of finding our system in different points of phase space. This density of probability contains all the information about fluctuations. The master equation, eqs. (5–7), has nonlinear coefficients in the case of adiabatic thermal explosion and its general analytical solution for the density of probability(3) is not of practical use. A useful analytical solution of the master equation is known for some approximate descriptions of the adiabatic thermal explosion without the inverse reaction.(3,6,10) In this paper we solve numerically the master equation for the systems with and without the inverse reaction. Although our results are limited to the small systems (in this paper we are concerned with the systems of 1000 molecules) they can give some insight into the behavior of real systems and they suggest why and where the phenomenological description of chemical reactions can fail.

The adiabatic thermal explosion, without the inverse reaction, has been studied numerically by the Brussels group,(3,6) but the data have been published for one model only. The published numerical data for the chemical explosion are more complete.(7) The purpose of this paper is to enlarge and enrich numerical data on the time evolution of the system that exhibits the adiabatic thermal explosion. We also study the problem of influence of the inverse reaction on thermal explosion. This problem has not been discussed yet.

Our paper is divided into two parts. In the next section we introduce the phenomenological and stochastic description of adiabatic thermal explosion together with the three-level model for chemical reactions. The discussion of the time evolution of the system for different values of parameters describing the adiabatic thermal explosion is presented in Section 3.

2. PHENOMENOLOGICAL AND STOCHASTIC DESCRIPTION OF THE ADIABATIC THERMAL EXPLOSION

The complete description of any exothermic reaction is very difficult as the heat is released during the reaction and mass and energy transport processes should be taken into account. In this paper we are concerned only with the stochastic effects in the kinetics of chemical reactions and we use a rather crude model of reaction. Our model of the thermal adiabatic explosion follows one proposed by Baras *et. al.*(3) We assume that the system is homogeneous so that the temperature is uniform in space. This means that relaxation is synchronous throughout the system and that we can neglect all transport processes within it. The assumption that the process is adiabatic permits us to neglect the exchange of energy with the surroundings. It leads to the direct relationship between the number of molecules of the substrate and the temperature of the system [eq. (1)], what significantly simplifies the model. However, the influence of fluctuations on the dynamics of the thermal explosion can be also studied without this assumption. The model of explosion in an open system has been presented recently by Nicolis, Baras, and Malek-Mansour.(8)

Let us consider the system composed of the substrate X and the product A. The relative energies of X and A are displayed in Fig. 1. We assume that the direct reaction $X \rightarrow A$ goes through the activated complex $(X \rightarrow A)^*$ with the activation energy u_o. It is obvious that in this model the activation energy of the inverse reaction $A \rightarrow X$ is $u_o + r_v$ where r_v is the heat of reaction $X \rightarrow A$. This model, called the three level model for the direct reaction only, was used in the paper of Baras *et al.*(3)

In the adiabatic system the conservation of energy relates the concentration of substrate $\bar{x}$ and the corresponding temperature of the system $T(\bar{x})$

$$c_v \cdot T(\bar{x}) + r_v \bar{x} = \text{const.} = c_v T_M = c_v T_i + r_v \tag{1}$$

where c_v is the specific heat at constant volume. T_M denotes the maximal temperature in the system, which could be approached when all the substrate is transformed into the product and T_i is the initial temperature of the system. Writing eq. (1) we assume that c_v and r_v do not depend on temperature.

The simplest example of the thermal explosion is the reaction $X \rightarrow A$. In this case the phenomenological kinetic equation is(3)

$$\frac{d\bar{x}}{dt} = -k_D[T(\bar{x})] \cdot \bar{x} \tag{2}$$

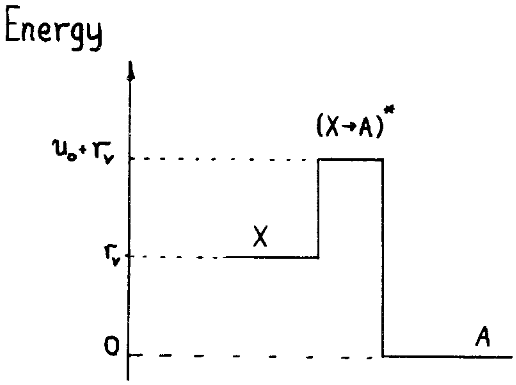

Fig. 1. The three level model of chemical reaction adopted in this paper: X, substrate; $(X \rightarrow A)^*$, intermediate complex; A, final product.

where $k_D(T)$ is the temperature-dependent rate constant. When the inverse reaction is taken into account, the phenomenological equation reads

$$\frac{d\bar{x}}{dt} = -k_D[T(\bar{x})] \cdot \bar{x} + (c - \bar{x}) \cdot k_I[T(\bar{x})] \tag{3}$$

where c is a constant depending on the initial conditions. We assume that the temperature dependence of the reaction rates for both direct and inverse reactions are given by the Arrhenius law

$$k_D(T) = k_{oD} \cdot \exp\left(-\frac{u_o}{k_B \cdot T}\right), \qquad k_{oD} = \text{const.} \tag{4a}$$

$$k_I(T) = k_{oI} \cdot \exp\left[-\frac{u_o \cdot (1 + r_v/u_o)}{k_B \cdot T}\right], \qquad k_{oI} = \text{const.} \tag{4b}$$

The phenomenological approach neglects the influence of fluctuations on the dynamics of chemical reaction. This effect can be taken into account by using stochastic methods. The information about fluctuations can be obtained from the $P(Y, t)$—the probability of finding just Y molecules of the substrate at time t.

It is well-known that the chemical reaction can be treated as a jump process.$^{(2)}$ Let us denote by $\mu(Y)$ the death rate (i.e., the transition rate from the state of Y molecules to the state of $Y-1$ molecules) and by $\lambda(Y)$ the birth rate (the transition rate for the inverse process). Then the following master equation can be written when both direct $X \to A$ and inverse $A \to X$ reactions are taken into account

$$\begin{aligned}(d/dt)\, P(Y, t) = {} & -[\mu(Y) + \lambda(Y)] \cdot P(Y, t) + \mu(Y+1) \cdot P(Y+1, t) \\ & + \lambda(Y-1) \cdot P(Y-1, t)\end{aligned} \tag{5}$$

where $\mu(Y) = Y \cdot k_D[T(Y/N)]$ and $\lambda(Y) = (N - Y) \cdot k_I[T(Y/N)]$. N denotes the number of molecules of X for $t = 0$. For the initial condition $P(Y, t = 0) = \delta_{Y,N}$, the phase space contains $N + 1$ elements and at two boundaries, $Y = 0$ and $Y = N$, the master eq. (5) has the form

$$(d/dt)\, P(N, t) = -\mu(N) \cdot P(N, t) + \lambda(N-1)\, P(N-1, t) \tag{6}$$

and

$$(d/dt)\, P(0, t) = \mu(1) \cdot P(1, t) - \lambda(0)\, P(0, t) \tag{7}$$

Equations (5–7) can be used also in the case when the inverse reaction is neglected, namely putting $\lambda \equiv 0$.

Now let us consider the influence of fluctuations on the kinetics of explosion. The general case of the transient bimodality induced by fluctuations was discussed by Frankowicz, Malek-Mansour, and Nicolis.(9) For the adiabatic thermal explosion it is quite easy to show that for any set of parameters of the reaction (u_o, r_v/c_v) and for any initial number of molecules N there exists an initial temperature T_i for which the behavior of the system is not deterministic. For simplicity we discuss the system without the inverse reaction, but similar argumentation can also be presented for the case when this reaction is taken into account. According to the stochastic approach the time $t_{Y,Z}$ of the transition from the state of Y molecules of X to the state of Z ($Z < Y$) molecules is equal to

$$t_{Y,Z} = \sum_{j=Z+1}^{Y} \frac{1}{\mu(j)} \tag{8}$$

As the temperature changes during the reaction it may happen that for a special choice of parameters of adiabatic thermal explosion the transition time $t_{N,N-K}$ ($K \ll N$) is much longer than the transition time $t_{N-K,0}$. This means that the induction period is very long, but when temperature increases, the reaction speeds up and the system approaches its final state very rapidly. In this case the fluctuations in the initial period have a great influence on the evolution of the system. For example, it can be shown very easily that when

$$T_i \cdot \left(T_i + \frac{1}{N} \cdot \frac{r_v}{c_v} \right) \ll \frac{u_o r_v}{k_B c_v} \cdot \frac{1}{2N \ln(N)} \tag{9}$$

then

$$t_{N,N-1} \gg t_{N-1,0} \tag{10}$$

which means that the system reaches its final state just after one molecule of X changes into A. Therefore the behavior of the system is stochastic because the time when the first elementary reaction takes place is fortuitous. Such a system cannot be studied with the use of phenomenological eq. (3); however, it can be well-described by the probability distribution $P(Y, t)$.

Usually for realistic values of parameters of the adiabatic thermal explosion, the inequality (10) leads to unrealistically small values of T_i. However, condition (9) is rather restrictive and the transient bimodality can also be observed with higher initial temperatures. Such cases are discussed in the next section.

3. THE NUMERICAL SIMULATION OF THE ADIABATIC THERMAL EXPLOSION

The time evolution of the probability distribution $P(Y, t)$ is determined by numerical solution of the master eqs. (5–7). These equations are integrated using the Runge–Kundt and the Merson methods.(4) Our calculations have been repeated for different time steps to check numerical stability. All numerical models discussed in this section have the same initial condition: $P(Y, t=0)=\delta_{Y,1000}$.

Adiabatic Thermal Explosion in the System Without Inverse Reaction

For numerical calculations we have chosen the following values of parameters describing the thermal explosion: $u_o/k_B=10000$, $r_v/c_v=1200$. In this point we follow Kondratiev and Nikitin(5) who discussed the adiabatic thermal explosion on the basis of phenoenological eq. (2) and the paper of Baras *et al.*(3) who investigated the stochastic model for such reaction. We have studied the time evolution of the probability distribution for three different initial temperatures $T_i=1100$ K, 800 K, and 600 K.

Figure 2 shows the time evolution of $P(Y, t)$ for the initial temperature $T_i=1100$ K. For this temperature there is no significant difference between the transition times in the initial period and in the region of explosion. The probability distribution has a Gaussian shape. This shape is preserved in time and the maximum of $P(Y, t)$ moves toward the stable state $Y=0$, which is located at the boundary of the phase space. The comparision of the results of the phenomenological equation with the results of the stochastic approach is shown in Fig. 3. For the initial temperature $T_i=1100$ K the time evolution of $\bar{x}$ is close to the $\langle Y/N\rangle(t)$ obtained from the stochastic model and also to the evolution of the maximum of $P(Y, t)$. It means that in this case the phenomenological descrition is in a good agreement with the stochastic one.

But when the initial temperature is lower, the behavior of the system characterized by the same u_o/k_B and r_v/c_v is completely different. Figure 4 shows the probability distribution for a few selected times for $T_i=600$ K. The probability distribution becomes more flat during its time evolution, but its maximum only slightly moves toward small values of Y. The second maximum of $P(Y, t)$ appears at $Y=0$ and the dispersion is many times higher then it was for $T_i=1100$ K. The time evolution of the probability distribution for $T_i=800$ K is very similar to that for $T_i=600$ K, but the first maximum is wider and its motion toward $Y=0$ is faster. Our results for $P(Y, t)$ for $T_i=800$ K are the same as published in Ref. 3, so we do not present them here.

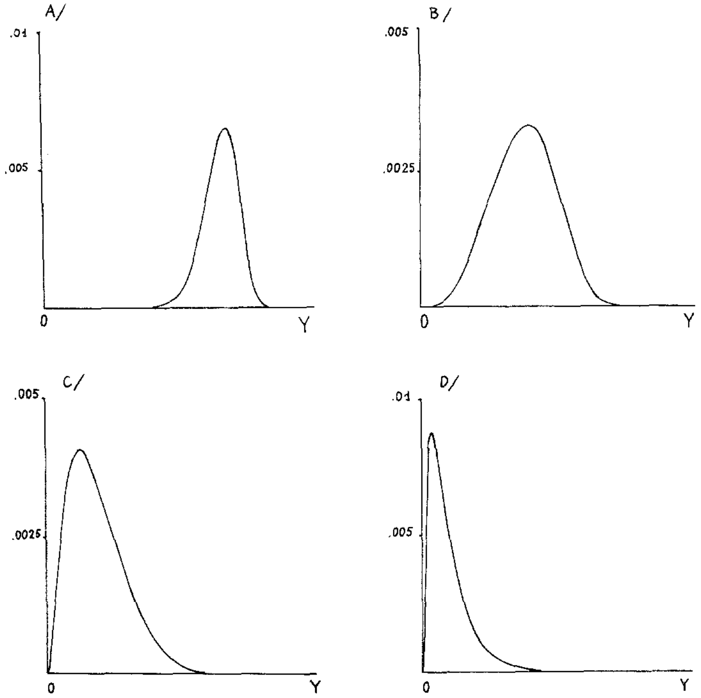

Fig. 2. The evolution of $P(Y, t)$ for high initial temperature of explosion $T_i = 1100$ K. (A) $t = 1167$, $\langle Y \rangle = 613$; (B) $t = 1297$, $\langle Y \rangle = 451$; (C) $t = 1470$, $\langle Y \rangle = 190$; (D) $t = 1556$, $\langle Y \rangle = 94$.

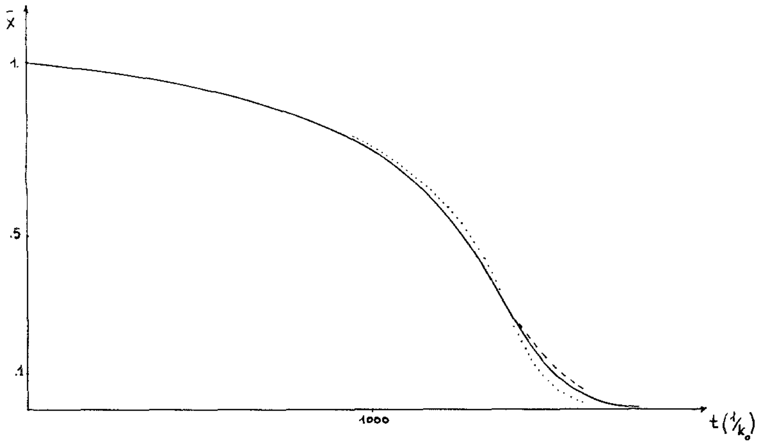

Fig. 3. The comparison of results of the phenomenological and stochastic approaches for high initial temperature $T_i = 1100$ K. Full line: the time evolution of the concentration of substrate $\bar{x}$ given by the phenomenological equation. Dashed line: the time evolution of the average value of numerical density $\langle Y/N \rangle$ obtained with the use of the probability distribution. Dotted line: the evolution of the maximum of $P(Y, t)$.

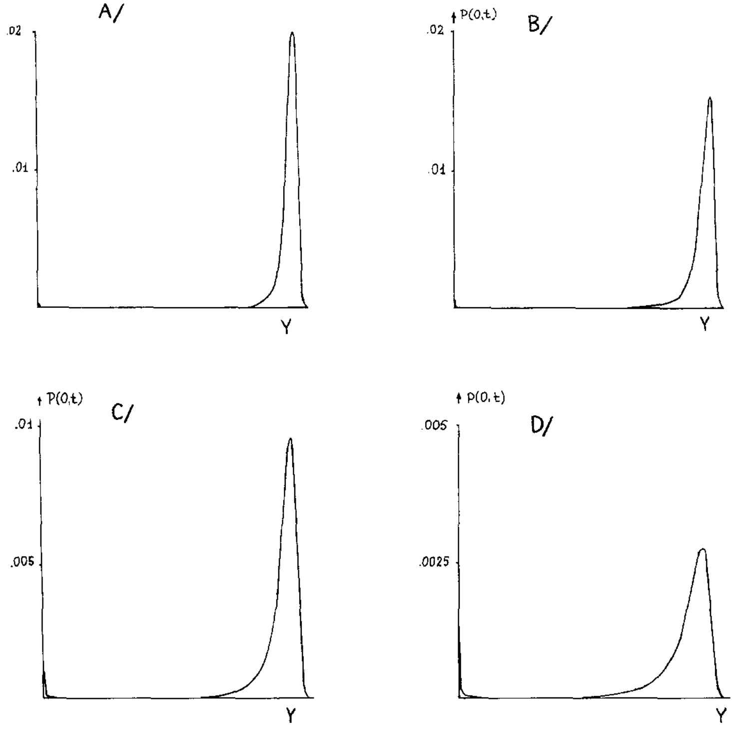

Fig. 4. The evolution of $P(Y, t)$ for low initial temperature of explosion, $T_i = 600$ K. (A) $t = 482231$, $\langle Y \rangle = 924$, $P(0, t) = 0.0086$. (B) $t = 507231$, $\langle Y \rangle = 896$, $P(0, t) = 0.026$. (C) $t = 567231$, $\langle Y \rangle = 731$, $P(0, t) = 0.17$. (D) $t = 657231$, $\langle Y \rangle = 297$, $P(0, t) = 0.64$.

The comparision of the results of the stochastic method with the results of the phenomenological approach for temperatures $T_i = 800$ K and $T_i = 600$ K is presented in the Figs. 5 and 6, respectively. It can be noticed that the phenomenological eq. (2) does not describe the time evolution of the maximum of $P(Y, t)$ nor the evolution of the average number density $\langle Y/N \rangle$. This result indicates that when the dispersion of the process is very high the phenomenological approach is meaningless.

The coexistence of two maxima of $P(Y, t)$ for the thermal adiabatic explosion ($T_i = 800$ K) was first observed in Ref. 3. However, in our calculations the second maximum appears just at $Y = 0$, whereas authors of the paper mentioned above (see also Ref. 6) suggested that the second peak of probability distribution first appears for Y close to zero and then moves to $Y = 0$ (compare Fig. 5 of this paper with Fig. 5 of Ref. 3 and Fig. 6 of Ref. 6).

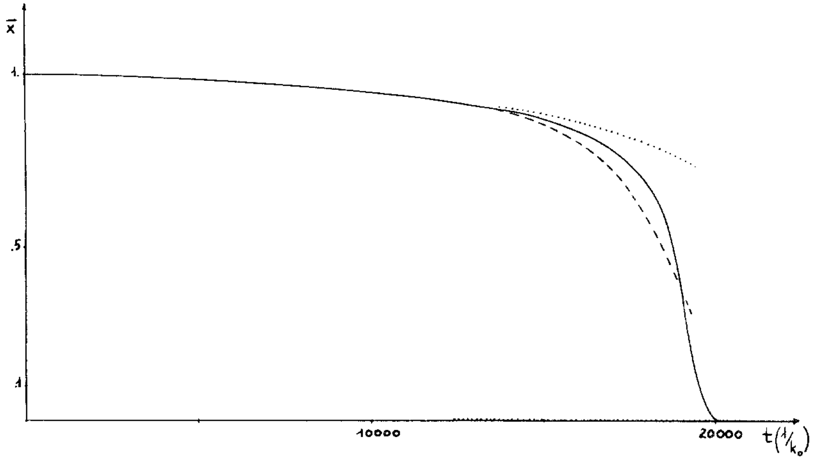

Fig. 5. The comparison of results of the phenomenological and stochastic approaches for the $T_i = 800$ K (notation as for Fig. 3).

Our calculations have been repeated for a few initial numbers of molecules of substrate and we have used different methods of numerical integration and different values of time step. The result that the second maximum appears at $Y = 0$ has been also obtained in the paper of de Pasquale and Mecozzi,(10) where the Poissonian representation technique has been applied for the solution of the master eq. (5–7) with $\lambda \equiv 0$.

Figure 7 shows the dependence of the dispersion of $P(Y, t)$ on the average numerical density of substrate $\langle Y/N \rangle$ for the system of 1000

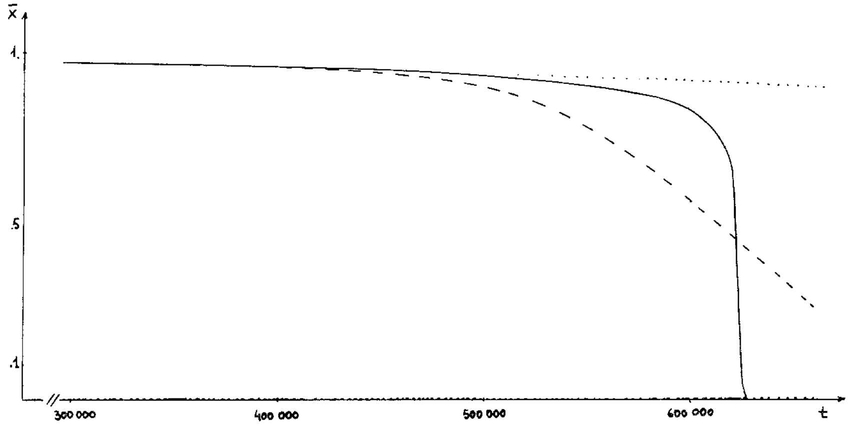

Fig. 6. The comparison of results of the phenomenological and stochastic approaches for low initial temperature ($T_i = 600$ K; notation as in Fig. 3).

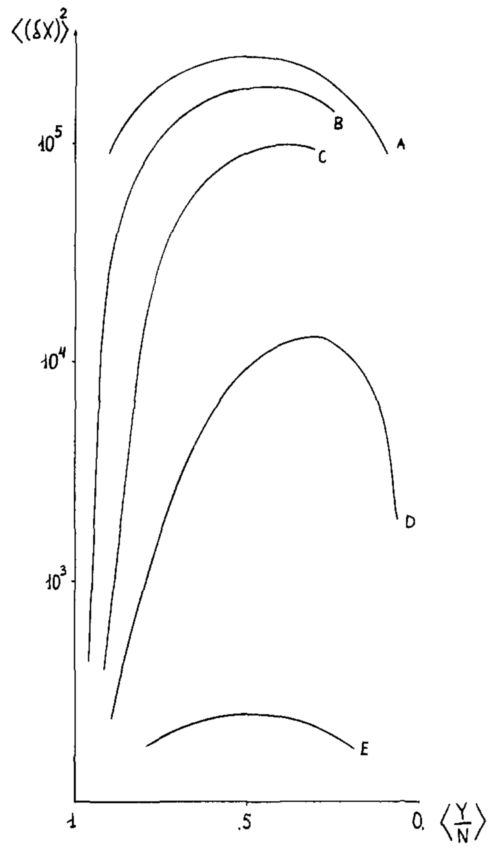

Fig. 7. The dispersion of $P(Y, t)$ as the function of the average numerical density for the processes without the inverse reaction. (A) the maxial value of dispersion. (B) $T_i = 600$ K. (C) $T_i = 800$ K. (D) $T_i = 1100$ K. (E) the process with $\mu(Y) = k \cdot Y$.

molecules. The dispersions of the processes presented in Figs. 3, 5, and 6 are compared with the dispersion of the reaction with the constant reaction rate and with the maximal dispersion of the probability distribution over the space of 1001 elements for a given $\langle Y/N \rangle$. The dispersion for adiabatic thermal explosion is many times higher than for the process with a constant reaction rate. This is the reason why any description, which uses an average number of molecules only (like the phenomenological one) can fail for the adiabatic thermal explosion.

Systems with the Inverse Reaction

A more realistic model of the adiabatic thermal explosion must take into account the inverse reaction $A \rightarrow X$. Here we present the numerical

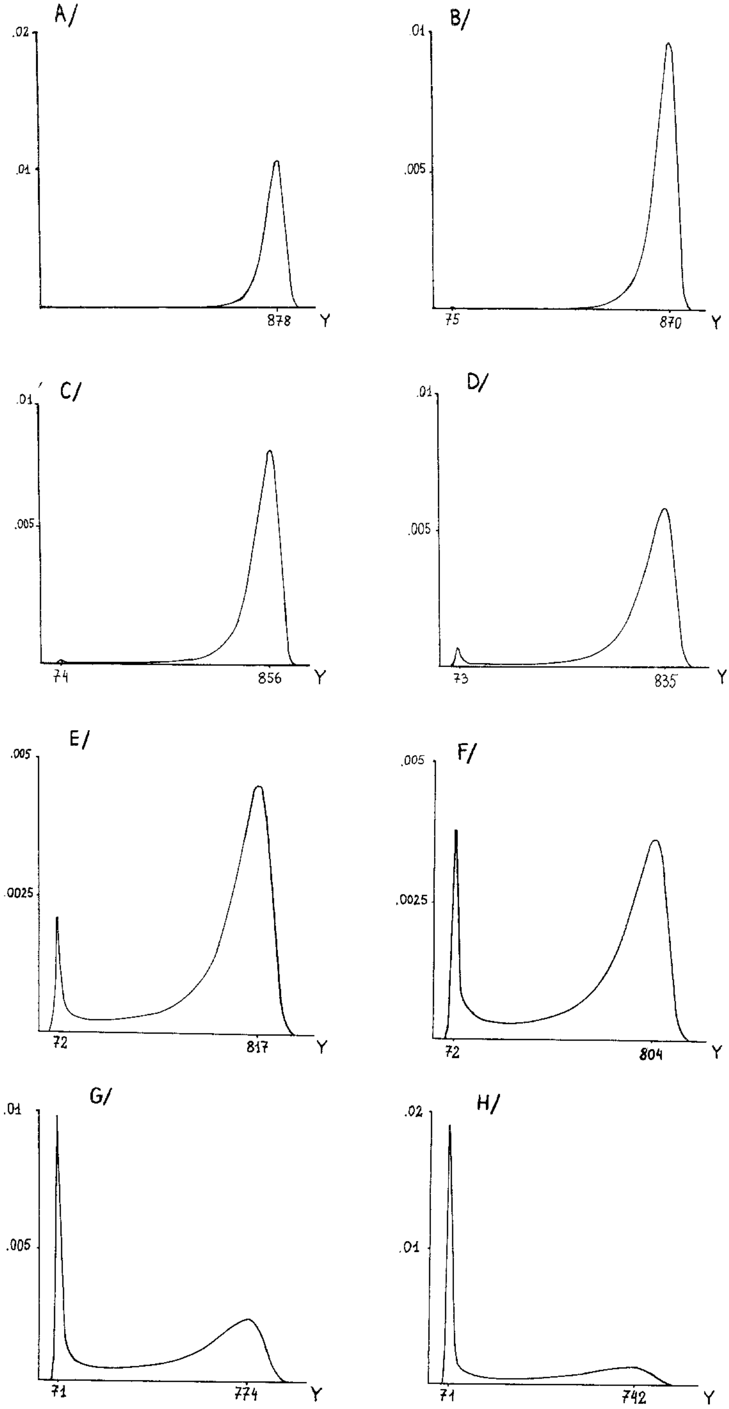

Fig. 8. The evolution of $P(Y, t)$ for the system with the inverse reaction $T_i = 800$ K. (A) $t = 15047$, $\langle Y \rangle = 853$. (B) $t = 15447$, $\langle Y \rangle = 837$. (C) $t = 16047$, $\langle Y \rangle = 805$. (D) $t = 16847$, $\langle Y \rangle = 743$. (E) $t = 17447$, $\langle Y \rangle = 673$. (F) $t = 17847$, $\langle Y \rangle = 615$. (G) $t = 18647$, $\langle Y \rangle = 479$. (H) $t = 19447$, $\langle Y \rangle = 337$.

results for the time evolution of the system of 1000 molecules obtained on the basis of the model with the inverse reaction, when the parameters of adiabatic thermal explosion are the same as in the first section: $T_M = 2000$ K, $u_o/k_B = 10000$, and $r_v/c_v = 1200$. We have chosen the same constant k_o in the Arrhenius law, eq. (4), for the direct and inverse reactions $k_{oD} = k_{oI}$. The activation energy for the inverse reaction is taken as 1.5 of the activation energy for the direct reaction. In the framework of the three level model it means that the heat of reaction is one-half of the activation energy for the direct reaction. Such choice of parameters is rather arbitrary, but it is useful from the numerical point of view as it gives the rate of reaction large enough to handle the calculations in a reasonable computing time.

In this case the stable point $x_s = 0.0689$ is far from the boundary of the phase space. Figure 8 displays the time evolution of the probability distribution. The first peak of $P(Y, t)$ has a long tail and the second peak appears due to the existence of a stable state. Although here the mechanism responsible for the transient bimodality—the large difference of time scales—is identical as for the case when the inverse reaction is neglected, the results are slightly different. The second maximum of the probability distribution first appears for Y/N slightly greater than the stable point and then moves toward it. This effect is caused by the inverse reaction, which produces the flow of probability toward large values of Y. Of course the probability distribution exhibits the Gaussian peak at x_s with the natural dispersion for time $t \to \infty$. It is also worthwhile to add that the evolution presented in Fig. 8 is similar to the time evolution of the probability distribution for the chemical explosion.[7]

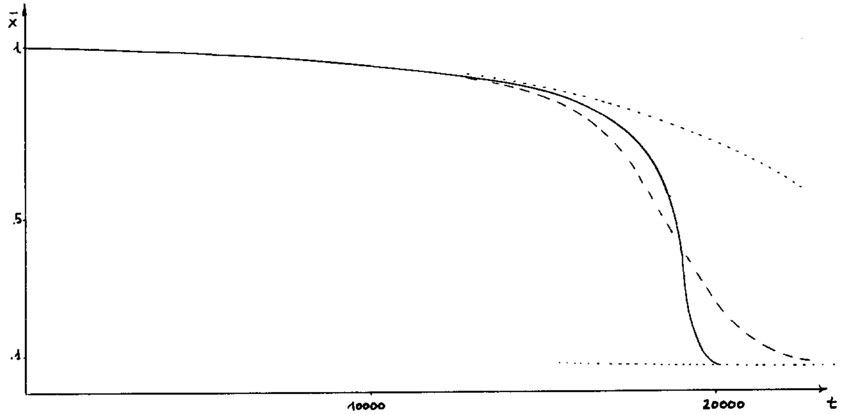

Fig. 9. The comparision of results of the phenomenological and stochastic approaches for the system with the inverse reaction $T_i = 800$ K. Notation as for Fig. 3.

Note (Fig. 8) that the dispersion of the probability distribution for the model with the inverse reaction is very large. It can be expected that the phenomenological description fails as it does in the case for the model without the inverse reaction. Numerical results confirm this opinion. Figure 9 shows the difference between the stochastic and phenomenological descriptions of the time evolution of the system with the inverse reaction. The results are very similar to those obtained in the first section for the same set of parameters of reaction.

4. DISCUSSION

Although the presented numerical results have been obtained for the system of 1000 molecules we believe that they are of more general value.

It has been shown that the phenomenological description of the adiabatic thermal explosion can fail when the dispersion of process is high. From the mathematical point of view the problem lies in the averaging of nonlinear function g. In the general case we have

$$\begin{aligned}\langle g(Y)\rangle &= g(\langle Y\rangle)+\frac{1}{2}\langle(\delta Y)^2\rangle \frac{d^2}{dY^2}\, g(Y)\Big|_{Y=\langle Y\rangle}\\ &\quad+\sum_{j=3}\frac{1}{j!}\langle(Y-\langle Y\rangle)^j\rangle\frac{d^j}{dY^j}\, g(Y)\Big|_{Y=\langle Y\rangle}\\ &\neq g(\langle Y\rangle)\end{aligned} \tag{11}$$

The relationship $\langle g(Y)\rangle = g(\langle Y\rangle)$, which is the basis of the phenomenological approach, is valid only when all the moments of $Y-\langle Y\rangle$ are negligible. As we have shown for any finite number of molecules, there exists a temperature [eq. (9)] such that the adiabatic thermal explosion is a process with high dispersion and so [cf., the second term of eq. (11)] the phenomenological description is meaningless. This conclusion can be true for any small system with nonlinear reaction rate and high dispersion, so we must be very careful with the use of phenomenological methods in such cases.

Our numerical results show that for both models discussed of the adiabatic thermal explosion, the system can exhibit transient bimodality behavior. However, the observed evolutions of the second maximum of the probability distribution are different, although in both cases the transient bimodality results from the difference of time scales in different regions of phase space. When the inverse reaction is neglected the second maximum appears at the stable state only. For the model with the inverse reaction the second peak emerges near the stable state and then moves toward it. This difference is caused by the flow of the probability distribution connected with the inverse reaction.

The model of adiabatic thermal explosion with the inverse reaction seems to be more realistic from the chemical point of view. Therefore, it seems to be a good starting point for the future development of the problem of stochastic theory of thermal explosions.

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