

## MONTE CARLO STUDIES OF CHEMICAL REACTIONS IN PLASMA FLOW

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This paper refers to the possibility of using the Monte Carlo method for the solution of problems connected with the utilization of plasma in chemical industry. The solution of the  $\text{CH}_4$  conversion in the  $\text{H}_2$  plasma flow is discussed in the present paper.

### РАСЧЁТ ХИМИЧЕСКИХ РЕАКЦИЙ В ПЛАЗМЕННОМ ПОТОКЕ МЕТОДОМ МОНТЕ-КАРЛО

В работе исследуется возможность применения метода Монте-Карло для решения проблем, связанных с использованием плазмы в химической промышленности. Обсуждается конверсия метана в водородном плазменном потоке.

#### I. INTRODUCTION

During the last fifteen years the Monte Carlo (MC) method has frequently been used also in plasma physics. This numerical method enables us to obtain in a facile way understandable solutions of very complicated problems regarding the elementary processes in the plasma and the kinetics of chemical reactions. By utilizing this method we can obtain an image of the change of velocity distribution in the mixing of two gases at different temperatures [1], we can model the motion of ions in the drift tube [2], determine the nonequilibrium velocity distributions and reaction rates in fast highly exothermic reactions [3], solve the relaxation processes in plasma [4], etc.

In the present paper we would like to show the possibility of the practical application of the MC method for the solution of macroscopical problems connected with the utilization of plasma in the chemical industry. The plasma temperature is higher than the temperatures used in classical chemistry, so that plasmachemical conversions of reagents take place much more quickly than in the current conditions prevailing in classical chemistry. For this reason it is necessary to know the optimal conditions of the product creation and the place of its maximal contents in the plasma flow. The knowledge of these facts enables us to choose the

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optimal conditions of the product creation and the place of the application of product preservation. These necessary dependences of the number density  $n$ , the temperature  $T$  and the flow speed  $v$  versus time  $t$  ( $n = n(t)$ ,  $T = T(t)$ ,  $v = v(t)$ ) can be obtained by the MC method. In this way it is possible to render the production of chemical materials by plasma chemistry more effective.

#### II. THEORETICAL MODEL

The MC method enables us to solve not only simple but also more complicated reactions of which the numerical or analytical solution is problematic.

The decomposition of  $\text{CH}_4$  molecules in the  $\text{H}_2$  plasma flow is an adequately complicated reaction. The shortened scheme of this decomposition is [5]



For the reaction constants  $k_i$  of these reactions the following formulae are valid according to [6]

$$k_1 = 4.5 \times 10^{13} \exp(-91000/RT) \text{ s}^{-1}$$

$$k_2 = 2.57 \times 10^8 \exp(-40000/RT) \text{ s}^{-1} \quad (2)$$

$$k_3 = 1.7 \times 10^6 \exp(-30000/RT) \text{ s}^{-1}$$

The conversion of  $\text{CH}_4$  to  $\text{C}_2\text{H}_2$  was carried out under these assumptions: The  $\text{H}_2$  plasma at the temperature  $T_0$  and the pressure  $p_0 = 10^5$  Pa flows with the velocity  $v$  in a sufficiently long tube. We do not take into consideration the radial distribution of the flow speed. The methane is injected into the plasma flow in a certain determined place. In this place the perfect mixing of  $\text{CH}_4$  and  $\text{H}_2$  molecules and the thermalization of these gases takes place. In this mixture there is 95 weight per cent of  $\text{CH}_4$  and 5 weight per cent of  $\text{H}_2$ . The reaction (1a) starts at the moment when the temperature of  $\text{CH}_4$  is equal to the plasma temperature. In this model we do not take into consideration the energy losses by therm conductivity or by friction.

In this case the flowing mixture of ideal gases can be described by the system of equations [7]

$$\frac{d(\rho v)}{dz} = 0 \quad (3)$$

$$\frac{dv}{dz} + \frac{1}{\rho v} \frac{dp}{dz} = 0 \quad (4)$$

$$\frac{dU}{dz} + \frac{1}{\rho v} \frac{d(\rho v)}{dz} + v \frac{dv}{dz} = 0 \quad (5)$$

$$p = n\kappa T, \quad (6)$$

where  $\rho$  is the density of the mixture,  $v$  the flow speed,  $p$  the pressure,  $T$  the temperature,  $n$  the number density of the mixture molecules,  $\kappa$  the Boltzmann's constant and  $U$  the specific internal energy. The following equations are also in force

$$\rho = \sum_{i=1}^5 \rho_i = \sum_{i=1}^5 \frac{N_i m_i}{V} \quad (7)$$

$$n = \sum_{i=1}^5 n_i = \sum_{i=1}^5 \frac{N_i}{V} \quad (8)$$

$$p = \sum_{i=1}^5 p_i \quad (9)$$

$$U = H - pV \quad (10)$$

$$\bar{n} = \sum_{i=1}^5 \bar{n}_i = \sum_{i=1}^5 \frac{n_i m_i v}{\rho v} = 1 \quad (11)$$

$$H = \frac{1}{\rho V} \sum_{i=1}^5 N_i h_i, \quad (12)$$

where  $m_i$  is the weight of the  $i$ -th molecule,  $N_i$ —the number density in volume  $V$ ,  $H$ —the specific enthalpy and  $h_i$  the enthalpy of the  $i$ -th molecule. From equations (3)—(6) we obtain

$$\rho v = K = \text{const.} \quad (13)$$

$$\frac{dv}{dz} + \frac{1}{K} \frac{dp}{dz} = 0 \quad (14)$$

$$\frac{dH}{dz} + v \frac{dv}{dz} = 0 \quad (15)$$

$$p = n\kappa T. \quad (16)$$

From Eq. (14) by using (4), (6) and (7) we express the relation for the calculation of the flow speed change during the chemical reaction

$$\frac{dv}{dz} = - \frac{\kappa v}{(Kv - \bar{p})} \left( \sum_i \frac{d\bar{n}_i}{dz} T + \sum_i \bar{n}_i \frac{dT}{dz} \right), \quad (17)$$

where  $\bar{p} = \bar{n}\kappa T$ . For the change of the temperature of the reacting mixture we obtain by modification of Eq. (12):

$$\frac{dT}{dz} = - \frac{(\bar{p} - Kv) \sum_i \frac{d\bar{n}_i}{dz} h_i + K\kappa T v \sum_i \frac{d\bar{n}_i}{dz}}{(\bar{p} - Kv) \sum_i \bar{n}_i \frac{dh_i}{dT} + K\kappa v \sum_i \bar{n}_i} \quad (18)$$

The temperature dependence of  $h_i$  is given by the empirical relation

$$h_i = h_i^0 + \frac{10^4}{N_A} \left( a_0 + \frac{a_1}{x} + a_1 x + a_2 x^2 + \dots + a_8 x^8 \right), \quad (19)$$

where  $h_i^0$  is the creation heat of the  $i$ -th molecule and  $a_j$  ( $j = -1, \dots, 8$ ) are coefficients from [8].

### III. MONTE CARLO MODEL

According to the method of periodical boundary conditions [9] we could replace the real flowing system by a relatively small number of particles. The application of the MC method to this small ensemble is possible. We worked with  $10^4$  particles. The flow chart of the MC model is in Fig. 1.

In a computer memory we reserved arrays for  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  molecules. 95 % of  $\text{CH}_4$  is characterized by 7050 digits 1 in the  $\text{CH}_4$  array. Then we set the initial values  $T_0$ ,  $v_0$ ,  $\bar{n}_{i0}$  ( $\sim$  indicates the equivalent memory number density) and  $a_i$  the coefficients for all components. We realized all the calculations in a cycle which was repeated approximately 150000 times.

The calculation procedure was as follows. We calculated the rate constants  $k_1$ ,  $k_2$ ,  $k_3$  for the initial temperature. These constants characterized the probability of the individual reaction  $P_i$

$$P_1 = k_1 / \sum_{i=1}^3 k_i, \quad P_2 = k_2 / \sum_{i=1}^3 k_i, \quad P_3 = k_3 / \sum_{i=1}^3 k_i. \quad (19a)$$

The reaction in each cycle is chosen by the common method of transformation of random numbers uniformly distributed in the (0, 1) interval to random variables with a discrete distribution defined by Eq. (14) [9].

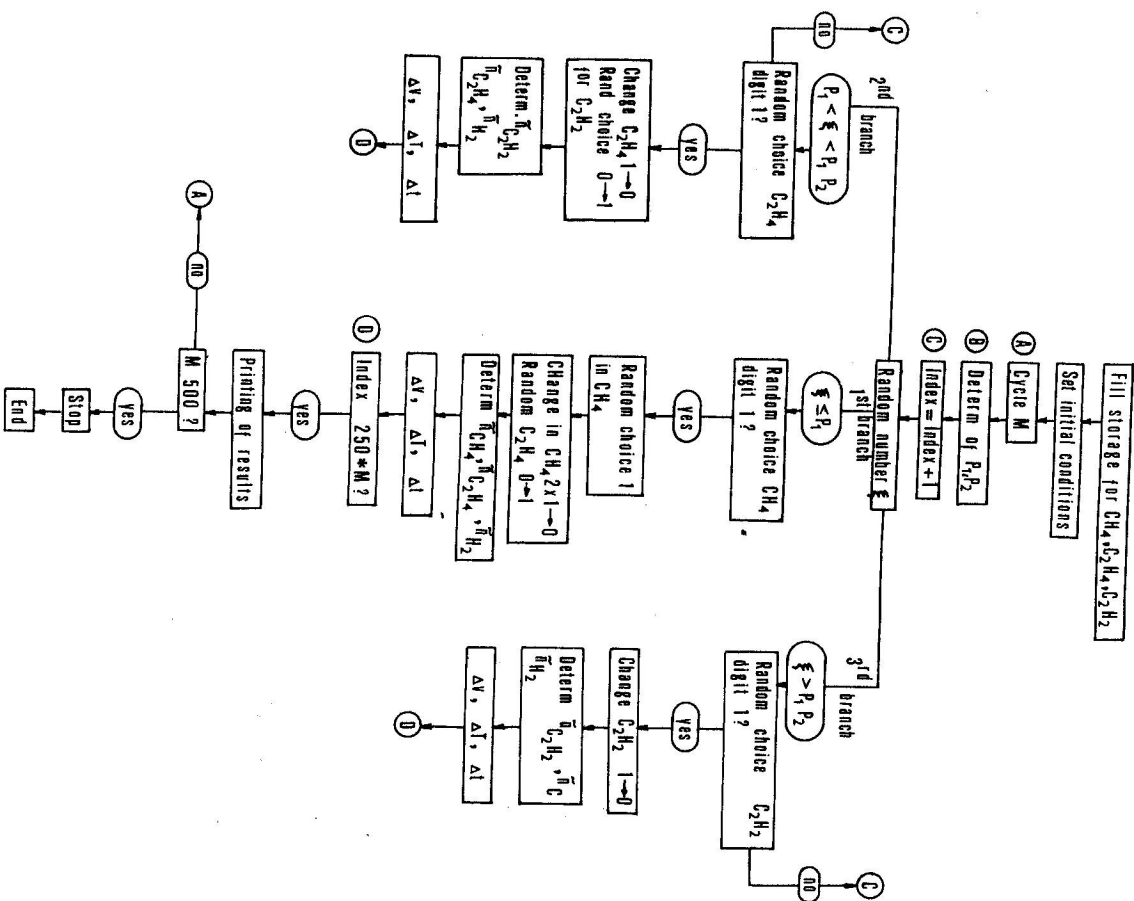
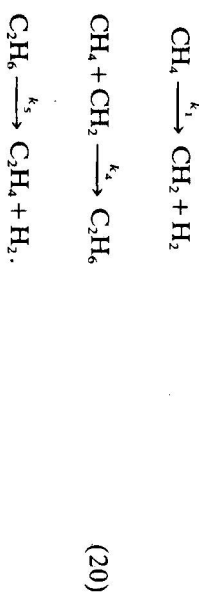


Fig. 1. Flow chart of the MC model for the  $\text{CH}_4$  conversion.

### III.1. Branch $2\text{CH}_4 \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2$

The real scheme of this branch is



Since  $k_1 \ll k_2, k_3$ , we can replace the scheme (20) by reaction (1a), which is fully described by the rate constant of the slowest reaction  $k_1$ . It means that this branch is the first order reaction.

While solving this branch we drew randomly the digits 1 or 0 from the array  $\text{CH}_4$ . The reaction did not take place if 0 was drawn. In such a case we went back to the beginning of the cycle. The reaction began when 1 was drawn and we randomly drew the second molecule  $\text{CH}_4$ . Then we calculated the change of enthalpy for this reaction at a given temperature and from (17) and (18) the change of the flow speed  $dv$  and the change of temperature  $dT$ . In the next cycle the choice of the reaction branch for the new temperature was repeated and new probabilities  $P_1, P_2, P_3$  were found.

### III.2. Branch $\text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2$

The structure of the calculation process in this branch is congruent with that of the first branch. The molecules  $\text{C}_2\text{H}_4$ , created in the first branch are placed randomly into the  $\text{C}_2\text{H}_4$  array. In this branch the  $\text{C}_2\text{H}_4$  molecules were randomly chosen from that array. Created  $\text{C}_2\text{H}_2$  molecules were randomly placed into the  $\text{C}_2\text{H}_2$  array. A new temperature  $T$  and the flow speed  $v$  were calculated from (17) and (18).

### III.3. Branch $\text{C}_2\text{H}_2 \rightarrow 2\text{C} + \text{H}_2$

In this branch

$$h_C = h_C^0 + h_{CT} + h_{C_{sublim}}$$

where  $h_{C_{sublim}}$  is the sublimation heat. The structure of this branch is congruent with other branch structures.

### III.4. The real time determination

The system of first order reactions (1) can be described by one rate constant

$$k_c = \sum_{i=1}^5 k_i \frac{n_i}{n} \quad (21)$$

For the first order reaction the number density is falling in accordance with the exponential law

$$n = n_0 \exp(-k_c t) \quad (22)$$

and so for the time  $t$  of the chemical reaction we have

$$t = \frac{1}{k_c} \ln \frac{n_0}{n} \quad (23)$$

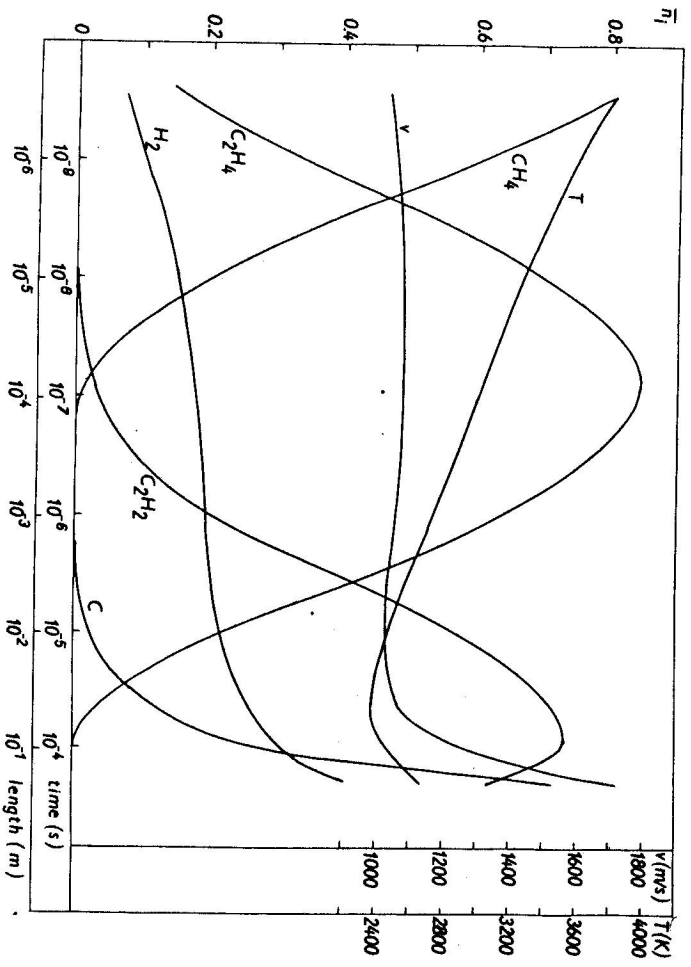


Fig. 2. The time dependence of the gas mixture temperature  $T$ , the flow speed  $v$  and the weight densities  $n_i$  for the  $\text{CH}_4$  conversion in the  $\text{H}_2$  plasma flow. Initial conditions:  $n_{\text{CH}_4} = 0.95$ ,  $n_{\text{H}_2} = 0.05$ ,  $T_0 = 4000$  K and  $v_0 = 1000$   $\text{ms}^{-1}$ .

According to [10] we obtained

$$t = -\frac{1}{k_c} \ln \frac{n_0}{n} \ln \gamma, \quad (24)$$

where  $\gamma$  is a random number from (0, 1). From (21) and (24) taking  $n_0 - n = 1$  we can obtain the relation for the calculation of the real time

$$t = -\frac{\ln \gamma}{k_c n_i} \quad (25)$$

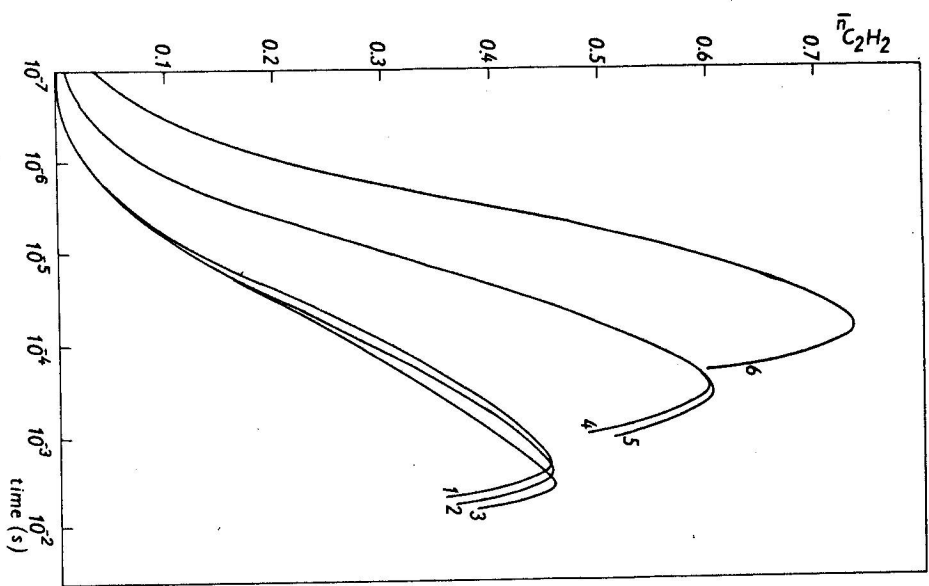


Fig. 3. Weight density  $n_{\text{C}_2\text{H}_2}$  versus time.

#### IV. RESULTS AND DISCUSSION

The results of the MC simulation are in Fig. 2. In this figure the complete results of a single calculation can be found. Fig. 2 reflects the complicated relations in the plasma flow with chemical reactions. We must realize that  $k_1 > k_2 > k_3$  at all ranges of temperature. The rate constants are comparable until the temperature reaches approximately 2200 K. It means that at the beginning the reaction (1a) is most effective, but when the number density of  $\text{CH}_4$  is markedly brought down, the number density of  $\text{C}_2\text{H}_4$  increases and the probability of the second reaction (1b) increases simultaneously. Then at the first phase of the  $\text{CH}_4$  conversion strongly endothermic reactions (1a) and (1b) are dominant. For this first phase of reaction a fast decrease of temperature (up to  $10^3 \text{ K s}^{-1}$ ) is characteristic. The third exothermic reaction (1c) is effective after  $2 \times 10^{-6} \text{ s}$  for  $T_0 = 4000 \text{ K}$ . The exothermicity of this reaction brings about the increase of temperature in the last phase of the reaction.

The change of the flow speed is very complicated. From (17) it is evident that the change of the flow speed does not depend only on the change of temperature but also on the change of the density of the mixture components.

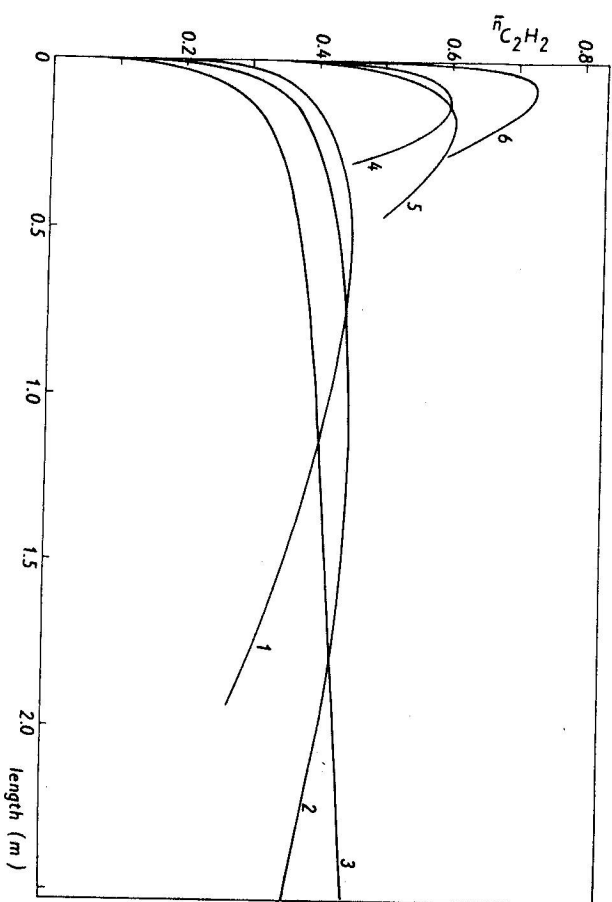


Fig. 4. Weight density  $n_{\text{C}_2\text{H}_4}$  versus length. 1 —  $T_0 = 3000 \text{ K}$ ,  $v_0 = 300 \text{ ms}^{-1}$ , 2 —  $T_0 = 3000 \text{ K}$ ,  $v_0 = 500 \text{ ms}^{-1}$ , 3 —  $T_0 = 3000 \text{ K}$ ,  $v_0 = 1000 \text{ ms}^{-1}$ , 4 —  $T_0 = 3500 \text{ K}$ ,  $v_0 = 300 \text{ ms}^{-1}$ , 5 —  $T_0 = 3500 \text{ K}$ ,  $v_0 = 500 \text{ ms}^{-1}$ , 6 —  $T_0 = 4000 \text{ K}$ ,  $v_0 = 1000 \text{ ms}^{-1}$ .

From Fig. 2 it is evident that the maximum of the  $\text{C}_2\text{H}_2$  number density appears later than the maximum of  $\text{C}_2\text{H}_4$ . The conservation of  $\text{C}_2\text{H}_2$  must be realized at the time  $8 \times 10^{-4} \text{ s}$  or at the distance 8.8 cm from the starting point (for  $T_0 = 4000 \text{ K}$ ,  $v_0 = 1000 \text{ ms}^{-1}$ ).

The influence of initial conditions of the acetylene number density in the plasma flow is shown in Fig. 3 and Fig. 4. The increase of the initial temperature leads not only to the increase of the product concentration but also to a considerable increase of the reaction speed. The increase of the flow speed enables us to achieve a more suitable space distribution of the individual products of the reaction. This fact allows a more facile application of the products conservation and also a not very exacting construction of plasma reactors.

For the calculation 4.5 minutes of computing time were required on a Siemens 4004.

#### V. CONCLUSION

In this paper we show the possibility of the application of the MC method to the solution of important plasmachemical problems. The decomposition of methane in the  $\text{H}_2$  plasma was solved by the Runge-Kutta method [5] but our calculations showed a better variability and adaptability of the MC method. Also the computing time for the MC calculations was shorter up to one order of magnitude in comparison with the Runge-Kutta method.

The program for the computer is applicable to the simulation of an arbitrarily complicated reaction scheme provided that the rate constants are known. When we are speaking of the kinetics of the  $\text{CH}_4$  conversion by the plasma way, it would be principally possible to extend the computer program and take into account also the creation of the molecules  $\text{C}_4\text{H}_4$  and  $\text{C}_4\text{H}_2$  and compute their content in the final mixture. The rate constants of creation and decomposition of these acetylene homologs are known [11]. In the MC calculation we work with a relatively small ensemble of particles and so it would be possible to take into consideration also the influence of energy losses by thermal conductivity and friction. The combination of the MC method and the method of optimization [11] seems very promising. In such a combination the MC calculation described above would substitute quite well the time-consuming, complicated experiments.

In the case when only experimental results are known it is possible to determine the rate constants of the individual reactions by fitting in the MC results.

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