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A Good Alternative to Numerical Methods of Integration for the Simulation of Chemical Kinetics: The Monte Carlo Method

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This paper illustrates the ways in which Monte-Carlo method provides a powerful tool for a simulation of complex reactions. New software using this method is described and tested on complex systems. The most important improvement in this software is the suppression of limitations on number of species and number of steps of the reaction mechanism.

Key Words: Monte Carlo method, Chemical kinetics, Simulation, Reaction mechanisms.

INTRODUCTION

Although we frequently find it in the simulation and modelling of the homogeneous, and more particularly heterogeneous[1–5], reacting systems, the Monte Carlo method is used for the treatment of particular cases and is not used as a general method as is the case for the numerical methods of integration which are used in many softwares[6–8]. However the simplicity of its principle and its flow diagram should support its implementation in the software of chemical kinetics simulation. The numerical methods of integration require a hard programming work and particularly if we must very the step of integration, which is often the case to reduce the computing time.

In this work, we describe the use of the Monte Carlo method as a general tool to simulate complex chemical systems. The method is implemented in user-friendly software with a powerful graphical interface simplifying the entry of the mechanisms and reducing the risk of errors which are frequent during the use of files with particular format. The most important improvement in this software is the suppression of limitations on number of species and number of elementary steps in the reaction mechanism. Its use does not require great knowledge in chemical kinetics.

The Model

Let us consider a chemical kinetic system governed by NR elementary reactions concerning NS species. The i-th elementary reaction has the form:

$$\sum_{j=1}^{3} (v_{ij}R_{ij} - w_{ij}P_{ij}) = 0 \quad (1)$$

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and its rate at a given moment is written as:

$$V_i = k_i \prod_{j=1}^{3} [R_{ij}]^{v_{ij}} \tag{2}$$

where k_i represents the rate coefficient; $[R_{ij}]$ the concentration of the j-th reactant and v_{ij} its stoichiometric coefficient, ($[P_{ij}]$) the concentration of the j-th product and w_{ij} its stoichiometric coefficient.

We also have for this system NS differential equations related to the NS species concerned in this mechanism. For the j-th species (S_j) we write:

$$\frac{d[S_j]}{dt} = \sum_{j=1}^{NR} x_{ij} V_i \tag{3}$$

with $x_{ij} = w_{ij}$ if S_j is identified with one of the products P_{ij}

$x_{ij} = -v_{ij}$ if S_j is identified with one of the reactants R_{ij}

$x_{ij} = 0$ if the S_j species is not present in the considered reaction

The kinetic treatment consists in solving the system of NS differential equations (3), *i.e.*, to find the expression of the concentration according to time for each species. In very rare cases, where the mechanism is very simple, it is possible to find analytical solutions for the system of differential equations. In all other cases numerical methods (Euler, Runge-Kutta, Gear . . .) must be used to produce approximate solutions. In this work, we will ignore the system of differential equations and use only the rate equation (2) to solve the problem in a probabilistic way by using the called Monte Carlo method whose flow diagram is given in Fig. 1.

At a given moment, the i-th reaction has a probability P_i of occurring which we can write at follows:

$$P_i = \frac{V_i}{\sum_{i=1}^{NR} V_i} \tag{4}$$

The sum of these probabilities being equal to one, we distribute them on the interval [0–1] by defining the new variable, Prob (i), as follows:

$$\text{Prob}(1) = P_1 \quad \text{and} \quad \text{Prob}(i) = \text{Prob}(i-1) + P_i$$

which gives $$\text{Prob}(NR) = 1$$

We ask the PC to generate a random number Rnd included in interval [0–1] and we compare it to the probabilities previously calculated. If it is located between the probabilities Prob (i – 1) and Prob (i),

$$\text{Prob}(i-1) < \text{Rnd} \leq \text{Prob}(i) \tag{5}$$

then it is the i-th reaction which will take place and we update the concentrations of the species concerned by this reaction as well as the reaction time. The

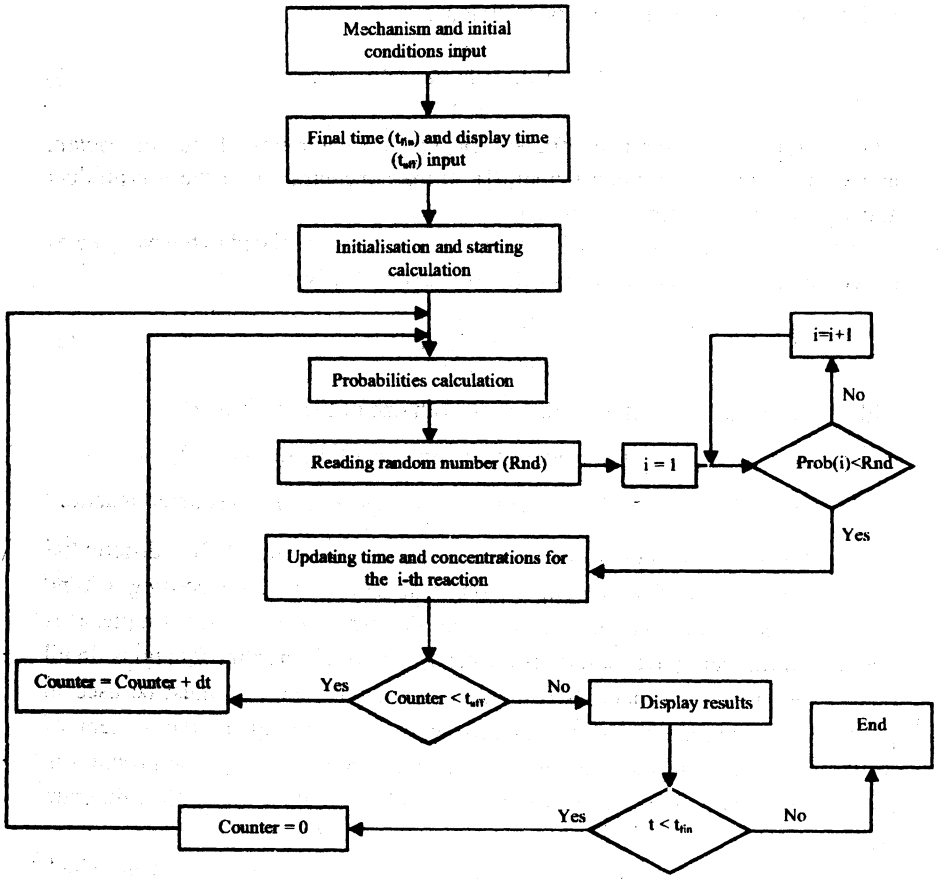

Fig. 1. Flow diagram of the simulation model based on Monte Carlo method

adjustment of the concentrations is done by the addition of w_{ij} entities to the product P_{ij} and the subtraction of v_{ij} entities of the reactant R_{ij}. Each entity corresponds to a certain concentration ΔC pre-calculated by corresponding to the weakest initial concentration C_{min}, a sample of N entities ($\Delta C = C_{min}/N$). The updating of the reaction time is done by taking account of this concentration (ΔC) and the rate of the selected reaction. Once these adjustments are made, we re-calculate the probabilities and then begin a second loop identical to the preceding one until a certain time t_{fin} (predefined by the user) is reached.

Description of the software

Our software works on PCs and under Windows environment and presents a principal window containing the main menu of the program and many secondary windows among which the mechanism input window, that of its recapitulation and that of the rate constants data. Fig. 2 shows the mechanism input windows inside the principal window. The graphical user-interface of the software is multilingual (French, English and Arabic). The choice of the language is done at compilation time of the program by using resource files of Visual Basic. Among

the functions of the menu of the program one finds those for opening, saving and creating files. The files are of two types: mechanism files (*.mcn) and result files (*.rsl). We can also find the functions of edition (edition of the result, the mechanism or the initial conditions) and the result display and impression functions (in tabular or graphic form). The principal task being the mechanism input, we tried to make it as simple as possible by presenting in the input window (Fig. 2) three fields for the reactants and three fields for the products. The reactants and products can be represented by their formulas, their names or by a symbolic letter, but two rules are to be observed:

- The same species must always be represented by the same symbol, for example CH4, ch4 and methane are three different symbols.
- This symbol should not start with a digit, because it will be regarded as stoichiometric coefficient.

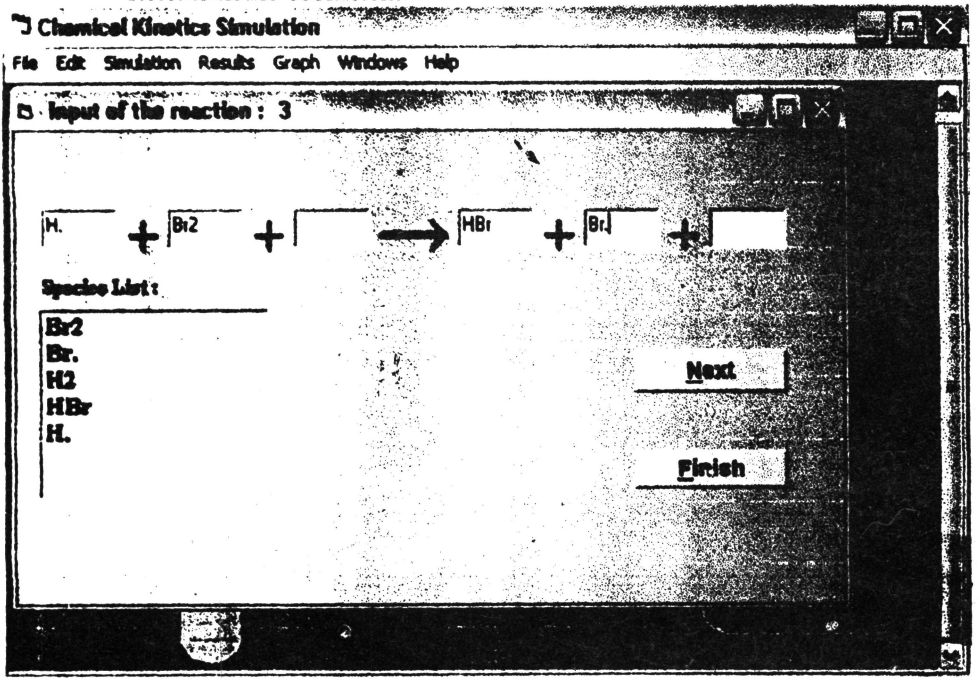

Fig. 2. The main window of our software with mechanism input window.

Once the mechanism is entered, a new window presents a recapitulation of all the elementary reactions entered for a last checking with the possibility of removing or modifying any reaction or additing a new one. The following stage is the input of the rate constants. These are entered through another window which presents three fields for the three Arrhenius parameters (A, n and E_a/R) according to the equation:

$$k = AT^n e^{\frac{E_a}{RT}} \tag{6}$$

When these parameters are given, the software automatically calculates the rate constants at the selected temperature. If the Arrhenius parameters are not

known, the value of the rate constant is entered in the A field (by default n and E_a/R are initialized to zero). The user finally enters the non-null initial concentrations (by default all the initial concentrations are initialized to zero). He selects a level of precision among the four proposed by the software, otherwise he enters the value of the precision which he wishes. He also chooses the final time, t_{fin}, of the reaction and the time between two consecutive points, t_{aff}, and then begins the simulation.

The simulation results are presented in a table whose first column represents the reaction time and the others the concentrations of all the species present in the mechanism. These results can be displayed in the form of curves (concentrations *vs.* time) or be copied in the clipboard of Windows for later use by another program such as Microsoft Excel or any other program.

Advantages of the software

The advantages and drawbacks of the various existing softwares of simulation of the chemical kinetics (KINFITSIM, KINSIM, KSIM, SIMKINE, FITALL, EASYFIT, . . .) are underlined in articles[7,8]. Compared with these software, our software offers the following advantages:

1. The user doesn't need experience in programming and has not to make any change in the source code of the program.
2. He doesn't need great knowledge in chemical kinetics: the software analyzes itself the mechanism and deduces the rate equations (2); these equations are derived and coded by hand in some software or are given in a special file, written in a specific description language[6].
3. He doesn't have to worry about the data file format; the data is entered interactively and the file is created automatically.
4. He fixes himself the final time of simulation and there is no limitation related to the number of loops of calculation.
5. He also fixes the number of points to be displayed by choosing an interval of time between each two consecutive points and can thus control the size of the result files.
6. He can exchange data with other programs *via* the Windows clipboard.
7. He can enter as many elementary reactions with as many species as he wants, without any limitation.

Tests of simulation

On a simplified mechanism: With the aim of checking the reproducibility and the precision of our results of simulation, we chose the traditional and simple mechanism:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

whose analytical solution is well-known:

$$[A] = [A]_0 e^{-k_1 t} \tag{7}$$

$$[B] = \frac{k_1[A]_0}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \tag{8}$$

$$[C] = [A]_0\left(1 - \frac{k_2 e^{-k_1 t}}{k_2 - k_1} + \frac{k_1 e^{-k_2 t}}{k_2 - k_1}\right) \quad (8)$$

This mechanism was simulated for the following values of k_1 and k_2: 0.9 and 0.7 (arbitrary unit) and for an initial concentration of A equal to 10 (arbitrary unit). We calculated the relative precision for each of the 3 species A, B and C by comparing the simulated concentrations with the exact values obtained from relations (8), (9) and (10). The average relative precision for the three species and each of the four levels of precision of the software is given in Table-1. It is noticed that even for the low level of precision, the relative error is lower than 1%. One notes here that the computing time varies considerably with the selected level of precision: for this example, it passes from a few seconds for the low precision to more than ten hours for the very high precision.

TABLE-1
AVERAGE RELATIVE PRECISION FOR THE VARIOUS LEVELS SUGGESTED BY THE SOFTWARE

Relative Precision (%)			
Low	Medium	High	Very high
0.97	0.78	0.06	0.01

By carrying out several simulations of this mechanism under the same conditions, we observed a very good reproducibility of the results.

On an oscillating reactional system: This kind of systems presents a certain challenge for researchers who want to simulate them; we chose to simulate the system described by Jungwirth[9] and concerning the photoautocatalytic oscillation of ozone. The choice of this system was dictated by two considerations:

- It is very recent, relative to the other known oscillating models (Lotka-Volterra, Brusselator, Oregonator . . . . [10–13]).
- It presents a certain analogy with the heterogeneous systems which we will comment on later.

This system is described in details in the Jungwirth's work[9] and we simly rewrite the mechanism prposed by the author with the initial conditions which he used in his calculations in order the compare our results with his. The author obtained his results by using a numerical integrator developed by Deuflhard[15].

The proposed mechanism consists of the following 11 elementary reactions:

$O_3 + h\nu \rightarrow 3O$	$k_1 = 10\ s^{-1}$	(R1)
$O + O_2 + M \rightarrow O_3$	$k_2 = 6.2 \times 10^{-34}\ cm^6\ s^{-1}$	(R2)
$O + Y \rightarrow$	$k_3 = 10^{-13}\ cm^3\ s^{-1}$	(R3)
$\rightarrow O_2$	$k_4 = 6 \times 10^{17}\ cm^{-3}\ s^{-1}$	(R4)
$\rightarrow Y$	$k_5 = 4 \times 10^{18}\ cm^{-3}\ s^{-1}$	(R5)
$Y \rightarrow$	$k_6 = 10\ s^{-1}$	(R6)

$$2O + M \rightarrow O_2 + M \qquad k_7 = 4.8 \times 10^{-33}\ cm^6\ s^{-1} \qquad (R7)$$

$$O_2 + h\nu \rightarrow 2O \qquad k_8 = 10^{-2}\ s^{-1} \qquad (R8)$$

$$O + O_3 \rightarrow 2O_2 \qquad k_9 = 8.3 \times 10^{-15}\ cm^3\ s^{-1} \qquad (R9)$$

$$O_3 \rightarrow \qquad k_{10} = 10^{-1}\ s^{-1} \qquad (R10)$$

$$O_2 \rightarrow \qquad k_{11} = 10^{-2}\ s^{-1} \qquad (R11)$$

The oxygen considered in this mechanism is triplet oxygen (^3O), except for the ozone molecule (O_3). Y is the species necessary to the creation of the oscillation. The species O_2 and Y are pumped in the reactional medium continuously by the reactions (R4) and (R5). The reactions (R1) and (R8) represent the photolytic dissociation (by UV) of the species O_3 and O_2. The reactions (R6), (R10) and (R11) represent the exit reactions for the species Y, O_3 and O_2. The initial conditions are given in Table-2.

TABLE-2
INITIAL CONCENTRATIONS OF THE VARIOUS SPECIES

$[O_3]_0$	$[O]_0$	$[O_2]_0$	$[Y]_0$
$10^{17}\ cm^{-3}$	$10^{14}\ cm^{-3}$	$10^{18}\ cm^{-3}$	$10^{17}\ cm^{-3}$

RESULTS AND DISCUSSION

The initial concentration of the moleular species M is not given explicitly in the paper[9], then we carried out several simulations with various values of this initial concentration while maintaining constant the initial concentrations of the other species (quoted in Table-2). We observe that the oscillation period varies with the concentration of M as shown in Table-3.

TABLE-3
VARIATION OF THE PERIOD AND THE AVERAGE O_2 CONCENTRATION AS FUNCTION OF M CONCENTRATION

[M] ($10^{18}\ cm^{-3}$)	3	4	5	6	7	8	9	10
Period (s)	15.6	10.8	10.2	10.1	9.4	8.6	7.6	6.4
$[O_2]$ ($10^{18}\ cm^{-3}$)	6.0	4.6	3.8	3.3	2.8	2.5	2.3	2.2

Table-3 suggests a value of [M] for which the period would be equal to 8 s, as the author of the mechanism quotes it, located between 4×10^{18} and $9 \times 10^{18}\ cm^3$. However such, a concentration would give an average value for the concentration of O_2 about $2.4 \times 10^{18}\ cm^3$, as Table-3 shows it, quite diferent from $4 \times 10^{18}\ cm^3$ given by the author. Another difference relates to the amplitude of the oscillations. We find an amplitude slightly higher for O_2 ($2.6 \times 10^{18}\ cm^3$ instead of $2.2 \times 10^{18}\ cm^3$), for O ($8.0 \times 10^{18}\ cm^3$ instead of $7.3 \times 10^{18}\ cm^3$) and for O_3 ($5.3 \times 10^{18}\ cm^3$ instead of $4.3 \times 10^{18}\ cm^3$). For the remainder, one observes a good similarity between our results and Jungwirth's[9], as shown in Fig. 3 which

represents the results obtained with the initial conditions of Table-2 with $[M] = 8 \times 10^{18}$ cm^3. For the sake of comparison, we used the same parameters for the axes as those used in Jungwirth's work[9].

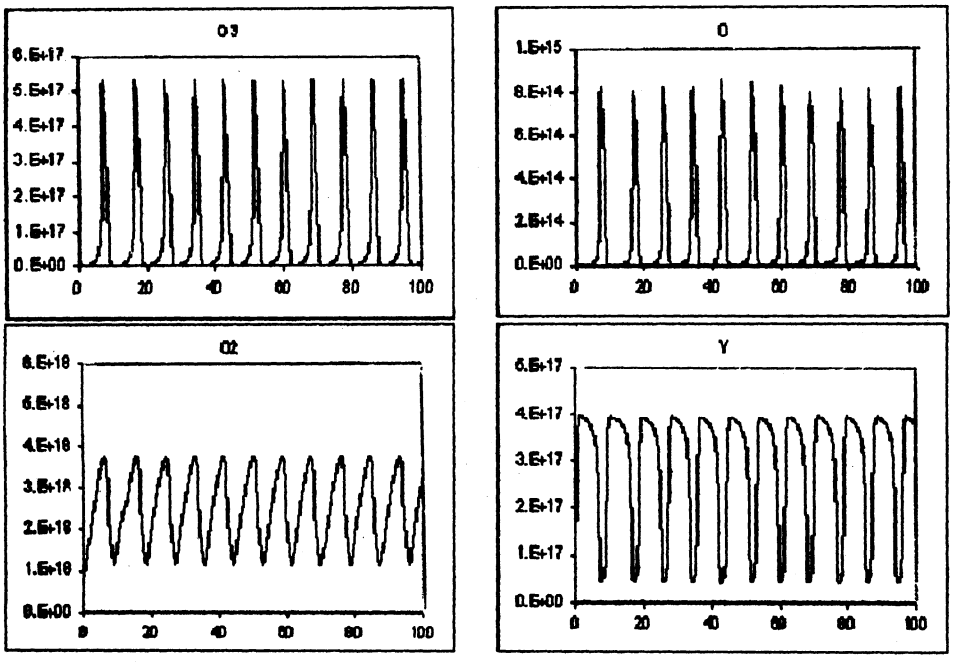

Fig. 3. Oscillation of the concentration of the species O_3, O_2, O and Y for the concentration $[M] = 8 \times 10^{18}$ cm^3 and the initial concentrations of Table-2

Analogy with the heterogeneous systems: In this part, the kinetic simulation of the heterogeneous systems can be done with our software without too many difficulties. Indeed, while considering the case of the reaction occurring in gas phase, with the participation of species at the condensed state (solid or liquid), the two reactions (R4) and (R5) would be similar to the reactions which represent the evaporation or the sublimation of these liquid or solid species. The reactions (R10) and (R11) would represent their condensations. In the case of the reaction taking place on the surface of a solid, the two reactions (R4) and (R5) would represent the adsorption of the gas species and the reactions (R10) and (R11) their desorption.

Conclusion

New user-friendly software is developed using the Monte Carlo method as an alternative to numerical integration methods to simulate any complex chemical mechanism. The most important improvement in our software is the suppression of the limitations on number of steps and number of species of the mechanism which are usually limited in other programs.

Future work will expand the software capabilities to simulate non-isothermal chemical systems and make it useful for thermal analysis studies.

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