

STOCHASTIC SIMULATION OF CHEMICAL REACTION BY
DIGITAL COMPUTER, I. THE MODEL

T. Sipos,¹ J. Tóth,² and P. Érdi¹

1. Danube Oil Company Computer Center,
2. Institute of Medical Chemistry, Semmelweis
University Medical School, Budapest

Received November 9, 1972

A stochastic model of complex chemical reactions is outlined. A discrete Markov process corresponds to the complex chemical reaction in the model i.e. the concentrations of the components are discrete quantities. The differences between the stochastic and deterministic models are discussed.

Описывается стохастическая модель сложных химических реакций. Дискретный процесс Маркова соответствует модели сложной химической реакции, т.е. концентрации компонентов являются дискретными величинами. Рассматриваются различия между стохастической и детерминистической моделями.

INTRODUCTION

Both deterministic and stochastic models are known to describe complex chemical reactions phenomenologically. The stochastic model of complex chemical reactions has been developed essentially by Rényi [1].

In the first part of this paper an extension of the stochastic model is presented. This model provides a framework for as many elementary reactions of as many components as desired under practically general conditions.

It should be pointed out that the stochastic model is more natural than the deterministic one.

As the solutions for possible models of even relatively less complex reactions cannot be presented in a closed form, which is also true for the deterministic model, one has to use approximate solutions or simulations. In fact we intend to show how to turn from the model described here to another permitting direct simulation experiment.

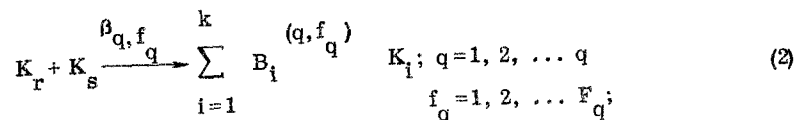
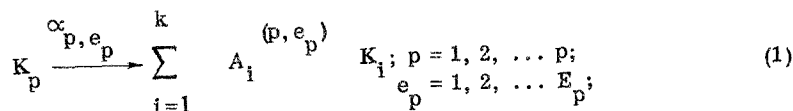
In the second part of the paper the computer realization of the model will be reported with some particular examples to prove that simulation experiments can be performed without the usual simplifying assumption of reaction kinetics.

A more detailed comparison of the deterministic and stochastic models, a full presentation of the program and an exhaustive list of references are given elsewhere [2].

II. THE STOCHASTIC MODEL

Let us take a vessel (e.g. a test tube, a reactor, a living organism, etc.) containing the components K_i in quantities $\xi_i(t)$ ($i = 1, 2, \dots, k$) at moment t . The system may be open or isolated, changes in pressure, temperature and volume are disregarded.

We suppose that only reactions involving one or two components (so called unicomponent and bicomponent reactions, ²) take place, i.e.



$$Q = Z(r, s) \quad (3)$$

where

α_{p, e_p} and β_{q, f_q} correspond to the reaction rate constants [1]

$A_i^{(p, e_p)}$ and $B_i^{(q, f_q)}$ are stoichiometric coefficients, i.e.

non-negative integers,

P is the number of components on the left-hand side of the unicomponent reactions,

Q is the number of component pairs on the left-hand side of bicomponent reactions,

E_p is the number of unicomponent reactions starting from the p -th component,

F_q is the number of bicomponent reactions starting from the q -th pair of components.

$Z(r, s)$ is the function giving the numbering of the bicomponent reactions starting from different pairs of components.

The following equations describe the change in the quantities of the components if a unicomponent reaction has taken place

$$\xi_i(t + \Delta t) = \xi_i(t) + A_i^{(p, e_p)} - \delta_{ip}, \quad (4)$$

For a bicomponent reaction we have

$$\xi_i(t + \Delta t) = \xi_i(t) + B_i^{(q, f_q)} - \delta_{ir} - \delta_{is}, \quad (5)$$

where

$$\begin{aligned} q &= Z(r, s), \quad i = 1, 2, \dots, k, \text{ and} \\ \delta_{ij} &= 0 \text{ if } i \neq j. \\ \delta_{ij} &= 1 \text{ if} \\ & i = j \end{aligned}$$

Further assumptions usually applied in the literature [3] are:

- time is treated as a continuous variable, while the quantities of the components as discrete ones, moreover it is assumed that

- the probability of any reaction different from those given by eqs. (1) or (2) is zero, and

- the probability that a reaction takes place is proportional to the time elapsed, to the quantities of components on the left-hand side and to the reaction rate constants,

- the probability that more than one reaction takes place is $o(\Delta t)^*$

* $o(\Delta t)$ is a quantity tending to zero when divided by Δt tend to zero, (i.e.

$$\lim_{\Delta t \rightarrow 0} \frac{o(\Delta t)}{\Delta t} = 0$$

Based on these assumptions, a relationship can be derived for the distribution. From this relationship the Kolmogorov equations can be deduced by dividing by Δt , with Δt approaching zero

$$\begin{aligned} \frac{\partial P(l; t)}{\partial t} = & \sum_{p=1}^P \sum_{e_p=1}^E \alpha_{p, e_p} (l_p + 1 - A_p^{(p, e_p)}) P(l - A^{(p, e_p)} + e_p; t) + \\ & + \sum_{q=1}^Q \sum_{f_q=1}^F \beta_{q, f_q} (l_r + 1 - B_r^{(q, f_q)}) (l_s + 1 - B_s^{(q, f_q)}) P(l - B^{(q, f_q)} + e_r + e_s; t) - \\ & - \left(\sum_{p=1}^P \sum_{e_p=1}^E \alpha_{p, e_p} l_p + \sum_{q=1}^Q \sum_{f_q=1}^F \beta_{q, f_q} l_r l_s \right) P(l; t) \end{aligned} \quad (6)$$

where

$$P(l, 0) = 1 \quad \text{if } l = D, \quad \text{or else } P(l, 0) = 0 \quad (7)$$

Here $l = (l_1, l_2, \dots, l_k)$, $0 = 1_i$, if $i = 1, 2, \dots, k$,

$$\xi(t) = (\xi_1(t), \xi_2(t), \dots, \xi_k(t)), \quad P(l, t) = P(\xi(t) = l),$$

$$A^{(p, e_p)} = (A_1^{(p, e_p)}, A_2^{(p, e_p)}, \dots, A_k^{(p, e_p)}),$$

$$B^{(q, f_q)} = (B_1^{(q, f_q)}, B_2^{(q, f_q)}, \dots, B_k^{(q, f_q)}),$$

$e_p = (\delta_{1p}, \delta_{2p}, \dots, \delta_{kp})$, i.e. e_p is the p -th

k -dimensional unit vector, and finally $D = \xi(0)$

III. STOCHASTIC VERSUS DETERMINISTIC MODEL

For the case when the number of the particles is finite, there does not exist a deterministic model. The description with differential equations, referred to as the deterministic model can only be an approximate calculation procedure, because the

solutions of the model are continuous functions, whereas the concentrations are discrete quantities,

On the basis of certain assumptions, which are, however, not always perfectly justified, it can be proved that the results obtained from the deterministic and the stochastic model essentially do not differ from each other.

The advantage of the stochastic over the deterministic model is especially evident in the analysis of so-called "small systems"[4]. Namely, if the number of particles of the components is small, the fluctuations taken into consideration by the stochastic model only, cannot be neglected even in the "zeroth approximation", because they are not superimposed upon the phenomenon but they represent the phenomenon itself.

IV. SIMULATION: THE TECHNIQUE OF SOLUTION

Equations (6,7) can be solved in very simple cases only. Therefore, a Markov chain is assigned to the original Markov process and this chain is simulated by the Monte Carlo method.

REFERENCES

- [1] A. Rényi: MTA AMI Közl., 2, 83, (1953)
- [2] P. Érdi, T. Sipos, J. Tóth: Magyar Kém. Folyóirat (in press)
- [3] D.A. McQuarrie, : J. Appl. Prob., 4, 413 (1967)
- [4] T.L. Hill: Thermodynamics of Small Systems, Benjamin, New York, Amsterdam, 1963