# STOCHASTIC SIMULATION OF CHEMICAL REACTIONS BY DIGITAL COMPUTER, II. APPLICATIONS

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The computer program aimed at the realization of a stochastic model of complex chemical reactions /1/ is described. Two applications of the program are given: (i) a reaction taking place on an adsorbent surface, and (ii) a reaction occurring under plasma conditions.

Описывается программа для ЭВМ, составленная с целью реализации стохастической модели комплексных химических реакций. Применение программы иллюстрируется на двух примерах: 1) реакция протекает на адсорбирующей поверхности и 2) реакция протекает в условиях плазмы.

## COMPUTER REALIZATION OF THE MODEL

In Part I /1/ a stochastic model of the chemical reaction - a Markoff chain - has been described. As mentioned there, the exact solution of the equations describing the model is usually impossible, so recourse has to be made to simulation experiments. In these experiments a reaction takes place with a probability proportional to the quantities of the reactants and to the reaction rate constants. To produce this probability a pseudo-random number is generated by the computer. After the reaction, which is to take place, ha been selected, the changes described by eqs. /4/ and /5/ of Ref. /1/ are accomplished. Essentially, this procedure is equivalent to observing directly the behaviour of a small fragment of the system.

The program has been written in PL/I language, the computer used is an IBM 360/40 model.

The output functions provided by the program are as follows:

- concentrations of all required component as functions of time $|\xi(t)|$,

- selectivity curves or trajectories / $\xi_i(\xi_j)$ /,

- entropy and its first and second derivatives as functions of time.

APPLICATIONS TO REACTION KINETICS

THEORETICAL CONSIDERATIONS

The results of the simulation experiments can be used either to support or to reject hypotheses concerning the mechanism of complex chemical reactions. To verify a conception based upon measurements is just possible as to investigate abstract chemical reactions (especially those of biological interest, e.g. reactions exhibiting oscillation, multivibration or a hysteresis loop) by the aid of simulation. Simulation experiments permit to eliminate simplifying assumptions such as "the principle of steady state", "rate determining step", " negligible reaction rate", etc.

As for checking the model, the reader is referred to paper /2/.

REACTION ON AN ADSORBENT SURFACE

Consider the reaction

$$A + B \underset{k_-}{\overset{k}{\rightleftharpoons}} R \qquad /1/$$

taking place on a solid surface. The mechanism of this reaction may be as follows

a/ adsorption of the reagents:

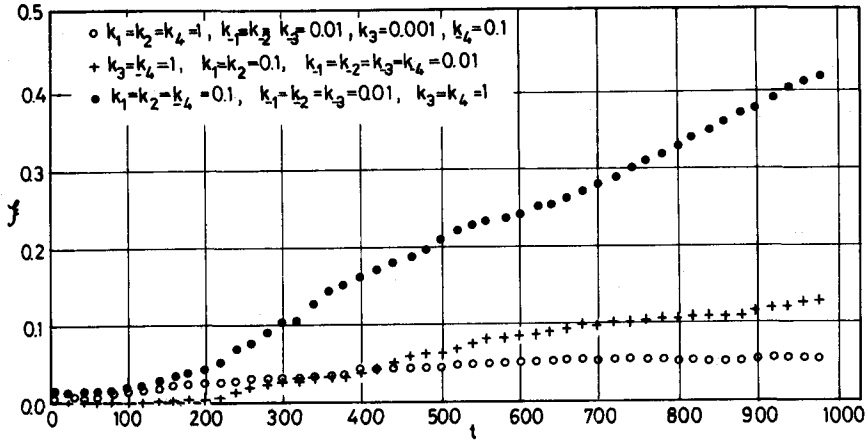$$A + s \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} As \qquad /2/$$

$$B + s \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Bs \qquad /3/$$

b/ adsorbed component A reacts with component B, the latter being in the fluid phase

$$As + B \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Rs \qquad /4/$$

c/ desorption of the product:

$$Rs \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} R + s \qquad /5/$$

In eqs. /2/-/5/, A, B and R are components in the fluid phase, s is a free adsorption site, As and Bs are adsorbed reagents and Rs is the adsorbed product.

When studying this reaction, it is often assumed that one of the steps is "rate determining", i. e. its rate is smaller than those of the others /4/.

By simulation the effect of the rate of the elementary steps on R/t/ can be investigated without this assumption /Fig. 1 /.


REACTION UNDER PLASMA CONDITIONS

In the last decade it has become especially important to investigate processes taking place at plasma temperature. Simulation may prove to be a useful method for studying reactions of this type.

Let us consider a relatively complicated hypothetic model similar to that presented in Ref. /5/:


| REACTION | TYPE OF REACTION | |
|---|---|---|
| $AB \rightarrow A + B$ | neutral dissociation | /6/ |
| $A + B \rightarrow AB$ | neutral association | /7/ |
| $AB + C \rightarrow AC + B$ | neutral exchange | /8/ |
| $AC + B \rightarrow AB + C$ | neutral exchange | /9/ |
| $B \rightarrow B^+ + e^-$ | formation of PAI | /10/ |
| $B^+ + e^- \rightarrow B$ | neutralization of PAI | /11/ |

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| | | |
|---|---|---|
| $AB \longrightarrow AB^{+} + e^{-}$ | formation of PMI | /12/ |
| $AB^{+} + e^{-} \longrightarrow AB$ | neutralization of PMI | /13/ |
| $A \longrightarrow A^{+} + e^{-}$ | formation of PAI | /14/ |
| $A^{+} + e^{-} \longrightarrow A$ | neutralization of PAI | /15/ |
| $A^{+} + BC \longrightarrow A + BC^{+}$ | atom-molecule charge-transfer | /16/ |
| $A + BC^{+} \longrightarrow A^{+} + BC$ | " " | /17/ |
| $AB^{-} \longrightarrow AB + e^{-}$ | neutralization of NMI | /18/ |
| $AB + e^{-} \longrightarrow AB^{-}$ | formation of NMI | /19/ |
| $AB^{+} + CD^{-} \longrightarrow AB + CD$ | mutual neutralization | /20/ |
| $AB + CD \longrightarrow AB^{+} + CD^{-}$ | collisional ionization | /21/ |
| $B + e^{-} \longrightarrow B^{-}$ | formation of NAI | /22/ |
| $B^{-} \longrightarrow B + e^{-}$ | neutralization of NAI | /23/ |
| $A + B^{-} \longrightarrow AB + e^{-}$ | associative detachment | /24/ |
| $AB + e^{-} \longrightarrow A + B^{-}$ | dissociative ionization | /25/ |

Abbreviations: N=negative, P=positive, A=atomic, M=molecular, I=Ion

Taking all the rate constants equal to unity, one obtains the following curve for $\alpha$, i. e. for the degree of dissociation of the system (Fig. 2 /:
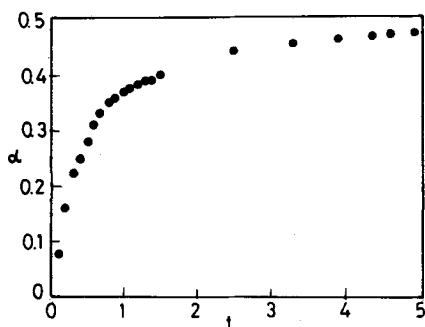


ACKNOWLEDGMENTS

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