Theoret. Chim. Acta (Berl.) 43, 165–174 (1976)

THEORETICA CHIMICA ACTA
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A Topological Stochastic Approach to the Study of Multidimensional Potential Energy Surfaces of Chemical Reactions

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In this article we propose a new approach for investigating the properties of multidimensional potential energy surfaces in chemical reactions, based on relations of each multidimensional surface to its one-dimensional image which is the chemical reaction tree. This approach makes it possible to find a common number of independent channels in chemical reactions for complex systems and to construct the probable models.

Key words: Multidimensional energy surfaces of chemical reactions - Topological and stochastic models

1. Introduction

In recent years quite a number of papers have appeared that are dedicated to the properties of two-dimensional potential energy surfaces of chemical reactions. The extension of such investigations to cases of greater dimension runs across substantial difficulties, since no visual image can be related with an n-dimensional surface when $n > 2$. The present paper aims at suggesting a new approach to describing multidimensional potential energy surfaces (PES) of chemical reactions. A multidimensional surface is represented by a certain one-dimensional (hence, visual) object called the surface tree.

As is known, variations of the mutual position of atoms in a molecular system are commonly described in terms of the potential energy function permitting a geometrical interpretation, namely as some surface in the configurational space [1]. Consider a potential energy function $U(q_1, \ldots, q_n)$ depending upon n generalized coordinates of the atoms participating in an elementary reaction act. Its corresponding geometrical image is an n-dimensional surface in the space of $(n + 1)$ dimensions. This PES corresponds to a definite electron term of the reactant system, at different configurations of the nuclei. Electron terms of the original reactive substances are assumed to be correlated with those of the products, which concept is known as the adiabatic approximation. Within the framework of the latter every state of the chemical system can be related to a representative point on the PES whose motion on the surface would describe the reaction [1].

According to this theory stationary points of the potential energy function $U(q_1, \ldots, q_n)$ are to be put in correspondence with definite molecular formations. Thus, local maxima and minima are related with the original substances and reaction products, and saddle points correspond to activated complexes. The chemical reaction is describ a motion of the representative point from the neighbourhood of the original react via the activated complex point and on to the point of the surface corresponding reactant products. However, at $n > 2$ the surface of $U(q_1, \ldots, q_n)$ cannot be visu and from the values of the stationary points no conclusion can be drawn on their position on the PES. Furthermore, an analytic expression for the potential energy tion is usually not known, which leads to the necessity of using tables. The tables $U(q_1, \ldots, q_n)$, calculated for all possible interatomic spacings, are cumbersome a to analyse, thus giving scarce information on the mutual position of the points. Ir connection there appears the problem of finding a class of mappings of the domai $U(q_1, \ldots, q_n)$ that would tie every n-dimensional surface to a certain one-dimens object. Such mappings should meet the condition of preserving the total number mutual arrangement of the function's stationary points. This demand invokes a to gical analysis of the PES. Indeed, possible reaction channels in the system, as well kinetic constants thereof, are determined by the number and mutual position of stationary points of $U(q_1, \ldots, q_n)$ and the values assumed there by the function: other words, by the topology of PES extreme points.

2. One-Dimensional Image of the Multidimensional Potential Energy Surface of th Chemical Reaction

The one-dimensional image of the multidimensional PES has been suggested by oı the authors (see paper [2]). The mathematical approach is based on the paper by A. Kronrod [3] dedicated to one-dimensional properties of functions of many vaı

Consider a function of two variables $U(q_1, q_2)$ possessing two local maxima and a saddle point. The surface of $U(q_1, q_2)$ and its plane map are represented in Fig. 1 is easy to see, equipotential levels of the surface (i.e. the lines $U(q_1, q_2) = t$) cons either one or several connected components. The aggregate of constant-level lines

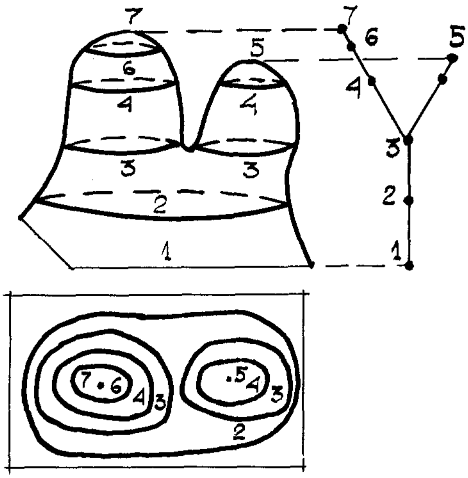

Fig. 1. The components of the $U(q_1, q_2$ sets

level set F_t of the surface. A representative point moving along component K of the level set F_t obviously has a constant potential energy t. From this point of view its dynamics on the constant-level line is trivial. Of interest are transitions between different energy levels. In order to describe the level set we resort to the following procedure. Each component of the set F_t will be associated with a single point on a plane, which points are to be ordered strictly in accordance with the components' energies. Kronrod's result [3] is as follows: If the function $U(q_1, q_2)$ is single-valued and continuous, then the point set on the plane is a tree. The construction of a surface tree is illustrated in Fig. 1. Local maxima of the surface are represented by end points 1 and 2 of the tree, the saddle point corresponding to the branch point 3.

Obviously enough, the level set concept remains valid with surfaces of higher dimension, hence the level set of a multidimensional surface can be similarly represented by a one-dimensional image, viz. a tree. Formally:

Let $U(q_1, \ldots, q_2)$ be a continuous potential energy function specified in a given n-dimensional domain $\mathscr{D}$. The level set F_t of $U(q_1, \ldots, q_n)$ is defined as a set of all points $x = (q_1, \ldots, q_n) \epsilon \mathscr{D}$ such that $U(x) = t$. The component K of the set F, containing point x, is the maximal connected subset $F_x \subset F$ containing that point. According to paper [3], for every function $U(q_1, \ldots, q_n)$ there exists a topological space T_U which is the one-dimensional tree $U(q_1, \ldots, q_n)$. Elements of the space T_U are components of the level sets. Topology can be introduced in T_U by the following considerations [3]. Let $M(K) \subset \mathscr{D}$ be an open set containing component K of the level set F_t. The sum of all the components completely contained in $M(K)$ (that are regarded as points in T_U) is a neighbourhood of element K in the space T_U. Then it can be easily proved that the system of open sets just introduced satisfies the axioms of a topoligical space. Further, it can be shown [3] that the space T_U constructed is a one-dimensional, locally connected continuum containing no homeomorphic images of the circle, hence a tree (any curve containing no simple closed curve is a topological tree).

Thus, the level set F_t is the function $U(q_1, \ldots, q_n)$ consists of equal-energy lines. Components of the set F_t are closed potential energy contours each corresponding to the same value of the functions $U(q_1, \ldots, q_n)$. Each component of the level set is related with a single point, different components being represented by different points on the plane. The points can be ordered in accordance with the growing values of $U(q_1, \ldots, q_n)$. The geometrical image obtained by mapping components of the level set on the plane is a tree. Hence, any n-dimensional PES of a chemical reaction can be associated with its corresponding tree [3]. All differential properties of the PES are completely ignored in the tree but topological properties of the surface that determine the number and mutual position of extreme points are retained.

The one-dimensional tree of a continuous function consists of a set of end points and a countable number of edges intersecting two by two at one point at the most, which is a branch point [3]. The number of branches intersecting at one point is called the vertex order [4]. The order of the end point is 1, that of a branch point is $\rho \geqslant 3$ [4]. As has been shown in [5], end points of a multidimensional PES correspond to initial reactants or products while branch points represent activated complexes.

An elementary act of a chemical reaction can be represented as a movement of the representative point along an oriented path between points E_0 (original configuration of reactant atoms) and E_t (mutual position of reactant atom products). All points of this path belong to constant-level contours. Since every component of the level set F_t is represented on the tree T_U, every path along the PES will have its corresponding path from one tree point to another.

3. Examples of Chemical Reaction Trees

Consider the PES of a system of three hydrogen atoms projected on a plane (Fig. 2a) [1]. The lines of constant energy are represented by closed curves. Closed contours homeomorphic with the circle correspond to regions of local maxima and minima of the potential energy function. Closed curves that are homeomorphic with the figure, which would result from gluing two points of the circle ("eights"), correspond to saddle points of the functions. Note that, by definition of the saddle point, the level next to that of the activated complex should have a greater value of potential energy. The surface shown in Fig. 2a has two valleys corresponding to the original substances and products, an energy saddle and a small depression on top of the saddle ("The Eyring Lake"). On the tree the valleys are represented by two end points, since the potential energy has local minima in those regions. The energy saddle is represented by a branch point. The third end point corresponds to the local maximum of the potential energy function. In this region the system completely dissociates into three separate hydrogen atoms. The fourth end point depicts the small depression on top of the saddle that corresponds to the formation of a H_3 complex.

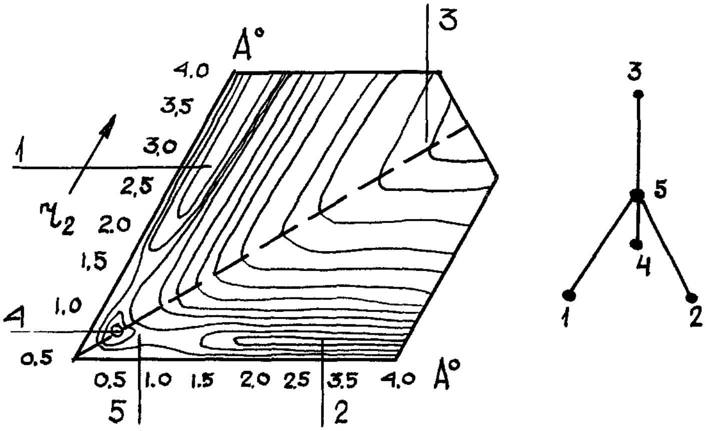

Fig. 2. The potential energy surface and tree for the orto-para hydrogen transition

Fig. 3 shows a plane map of the PES and the tree of tautomeric rearrangements for a pair of nitrogenous bases (guanine–cytosine) [6]. Points 1, 3, 7 and 8 correspond to the four possible tautomers in the guanine–cytosine system, points 2, 4 and 6 represent activated complexes and point 5 shows the state of the system with no hydrogen bond.

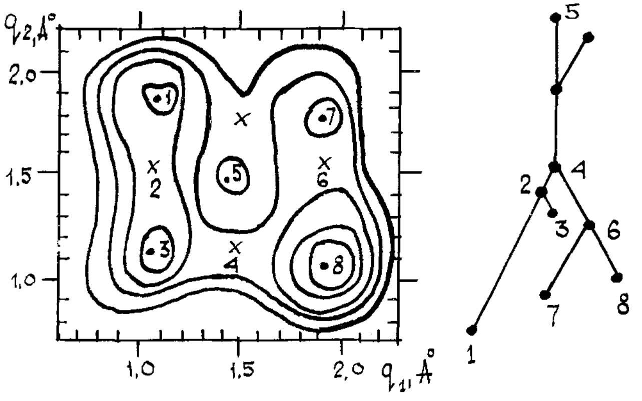

Fig. 3. The PES and tautomeric rearrangements tree for the guanine–cytosine system

The examples considered illustrate the general approach to constructing the reaction tree. If the number of generalized coordinates is $n > 2$ and the PES is specified with a table, there arises the problem of constructing the tree from the knowledge of numerical values of the potential energy function. Corresponding techniques will be described in another paper.

4. Non-Adiabatic Reaction Model

Using the concept of the PES tree one can put forward a model for non-adiabatic reactions [2, 7]. Such reactions are characterized by a relatively high probability of transitions between potential energy surfaces of different electron terms in the reactant system. A non-adiabatic reaction can be described by an ensemble of surfaces representing linearly independent functions $U_0, U_1, \ldots, U_s$ ordered in accordance with the growth of total energy value. Each integer value of the subscript s corresponds to a term with some constant magnitude of the system's total energy. A non-adiabatic transition is described by a "jump" of the representative point from one surface to another [1]. Hence, any set of non-adiabatic reactions can be described with a "pack" of s planes placed one under another (Fig. 4), each of them carrying a tree of $U_i(q_1, \ldots, q_n)$. The system's representative point moves during a non-adiabatic reaction along a path that includes points of the tree lying within different planes, with "jumps" between the planes. Presumably, transitions from one plane to another are most probable at branch points (activated complexes). If so, then the description of non-adiabatic reactions in terms of trees on a "pack" of planes is determinate, in the sense that there is only a finite definite number of transitions between the planes.

Every path of the representative point corresponds to a chemical reaction consisting of a finite number of elementary acts. Suppose all the reactions in the chemical system have equal probabilities, hence, the probabilities of the corresponding paths are also equal. An assumption like this implies equal constants for all the reacitons conceivable, which can be true only with rigid limitations on the constants of the elementary acts (e.g. reactions with either infinite or infinitesimal constants) [7].

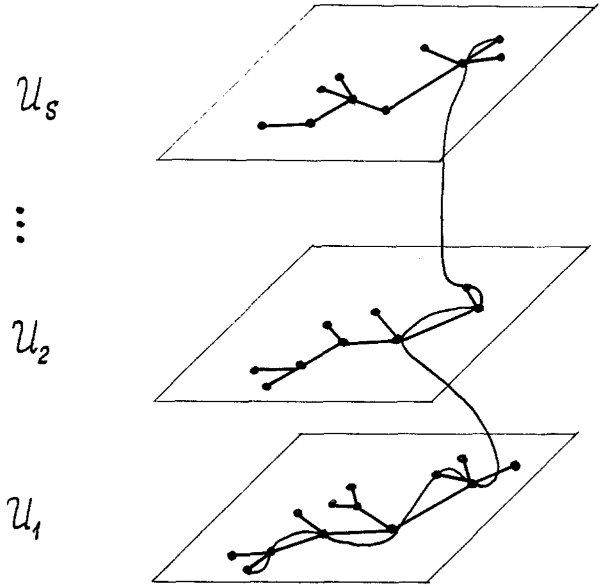

Fig. 4. The non-adiabatic reaction model

Let us introduce statistical weights for every non-adiabatic reaction [8], namely

$$P_i(E_0, E_i) = \frac{n(E_0, E_i)}{N(E_0, E)} \tag{1}$$

Here $n(E_0, E_i)$ is the number of all essentially different paths[1] from a fixed stationary point E_0 to a given point E_i and $N(E_0, E)$ is the number of essentially different paths from E_0 to any other stationary point E. If the total number of points belonging to the trees in the planes considered is r, then

$$\sum_{i=1}^{r} P_i(E_0, E_i) = \sum_{i=1}^{r} \frac{n(E_0, E_i)}{N(E_0, E)} = 1 \tag{2}$$

One can see from Eq. (2) that the value P_i defined by Eq. (1) represents a statistical weight. Consider, for instance, a non-adiabatic reaction [7] determined by two surfaces U_1 and U_2, with the numbers of stationary points m_1 and m_2, respectively. The number of essentially different paths leading from point E_0 of the first tree T_{U_1} to an arbitrary point E of the same tree, can be calculated by the formula

$$N(E_0, E) = (m_1 - 1)(m_2 - 2)^{k_{12}}(m_2 - 1)^{k_{12}} \tag{3}$$

Here k_{12} is the number of "jumps" made by the representative point between the surfaces U_1 and U_2. The path leading from the initial point and then back to it again

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[1] Two paths are essentially different if one of them contains at least one stationary point not belonging to the other.

has been excluded. The total number of all different paths between E_0 on T_{U_1} and a fixed point E_i on the same tree equals

$$n(E_0, E_i) = (m_1 - 2)^{k_{12}}(m_2 - 1)^{k_{12}} + k_{12} \tag{4}$$

The last term in Eq. (4) reflects the fact that there is only one "jumpless" path on T_{U_1} connecting E_0 with E_i.

Taking into account Eqs. (3) and (4) one can write the statistical weights for the class of non-adiabatic reactions specified by the surface pair U_1 and U_2, viz.

$$P_i(E_0, E_i) = \frac{1}{m_1 - 1} + \frac{1}{(m_1 - 1)(m_1 - 2)^{k_{12}}(m_2 - 1)^{k_{12}}} \tag{5}$$

The probabilistic model suggested here for non-adiabatic reactions can be easily extended to the case of s excited states $U_1, U_2, \ldots, U_s$ with $m_1, m_2, \ldots, m_s$ being the number of stationary points, respectively. Transition probability to the first excited state can be defined as in Eq. (5) [7]:

$$P_{12} = \frac{1}{m_1 - 1} + \frac{k_{12}}{(m_1 - 1)\prod_{i=2}^{s}(m_i - 1)^{k_{ij}}(m_{i-1} - 2)^{k_{ji}}} \tag{6}$$

with k_{ij} denoting the number of non-adiabatic transitions between the planes i and j, $k_{ij} = k_{ji}$, $j = i + 1$.

5. Kinetic Models on Chemical Reaction Trees

The existing chemical kinetics [9, 10] are developed independently of PES properties. In the activated complex theory, variations with time of the reactant molecule concentrations are not considered. In this connection we come to the problem of constructing a kinetic model of the chemical reaction, connected with the multidimensional PES. Complementing the postulates of activated complex theory with some proportions concerning the system's dynamics one can obtain kinetic equations. The PES tree concept has proved most useful for constructing kinetic models of chemical reactions characterized by multidimensional PES's [11 and 12].

The space of stationary points of the PES (tree vertices) can be considered as a discrete space of states of the chemical system. By the state of the system we mean the relative positions of the reactant atoms $(q_1, \ldots, q_n)$ at which the potential energy function assumes stationary values E. We will now define the probability function $P_{ij}(\tau, t)$ on the one-dimensional tree of the potential energy function. Should the system be in state E_i at the moment τ_T, the probability of it coming to state E_j at the moment t is $P_{ij}(\tau, t)$. According to the definition of the probability function [8].

$$P_{ij}(\tau, t) \geqslant 0, \qquad \sum_j P_{ij}(\tau, t) = 1 \tag{7}$$

Let the value of the probability function $P_{ij}(\tau, t)$ at $t > \tau$ be completely determined by the state E_i and be independent of the states at preceding moments of time. We then have [8]

$$P_{ij}(\tau, t) = \sum_k P_{ik}(\tau, s) \cdot P_{kj}(s, t) \tag{8}$$

where $P_{ik}(\tau, s)$ is the probability of the system being found in state E_k at the moment s', on the condition that it was in state E_i at the moment τ. The definition of $P_{kj}(s, t)$ is similar. Such a process is known as the Markov process [8].

We will further suppose that the motion of the representative point along the PES tree conforms to the following postulates:

1) Only such changes can take place in the system that correspond to transitions from a stationary point of the tree to closest neighbour points;
2) transition probability functions are uniform in time, i.e. $P_{ij}(\tau, t + \tau) = P_{ij}(t)$;
3) if at some moment t the system's state was E_j, then the probability of a transition to a "neighbouring" state E_i over time period $(t, t + \Delta t)$ is $k_{ij}\Delta t + o(\Delta t)$ where k_{ij} is the process constant, $o(\Delta t)$ denoting higher-order small terms;
4) the probability of more than one change of state in the system over time $(t, t + \Delta t)$ is a value of the order $o(\Delta t)$.

These postulates yield the following differential-difference Kolmogorov equations [8] for the transition probabilities

$$P'_{ij}(t) = \sum_n k_{nj} P_{in}(t) \tag{9}$$

where $k_{nn} = -\sum_j k_{jn}$, with the summation meaning over all points j adjacent to point n.

Unfortunately, the probabilistic model considered here does not allow one to explicitly take into consideration the PES parameters, since the transition probabilities depending on these are in most cases unknown. At the same time, knowing the number of reaction channels on the multidimensional PES (which can be determined from the tree), one is able to construct correctly the Markov process and determine the summation subscripts in the Kolmogorov equation (9) strictly in correspondence with the topology of the stationary points distribution. Construction of the surface tree and the Markovian theory could be united within a single coherent logical scheme, should one know the probabilities of transitions between neighbouring stationary points.

As an example of the application of the probabilistic model, consider the motion of a representative point along a tree associated with a first-order reversible reaction $A \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} B$ [11]. Let the representative point make transitions only from the states (E_1, E_2) corresponding to original substances and products. The differential-difference equations for that case become

$$\begin{aligned} P'_{11}(t) &= k_{21}P_{12}(t) - k_{12}P_{11}(t), \\ P'_{12}(t) &= k_{12}P_{11}(t) - k_{21}P_{12}(t), \\ P'_{21}(t) &= k_{21}P_{22}(t) - k_{12}P_{21}(t), \\ P'_{22}(t) &= k_{12}P_{21}(t) - k_{21}P_{22}(t). \end{aligned} \tag{10}$$

Let us compose a stochastic matrix[2] of the solutions to equation set (10):

$$P_t = \begin{pmatrix} P_{11}(t) & P_{12}(t) \\ P_{21}(t) & P_{22}(t) \end{pmatrix} =$$

$$\begin{pmatrix} \dfrac{k_{21} + k_{12}\exp[-(k_{12} + k_{21})t]}{k_{12} + k_{21}} & \dfrac{k_{12}(1 - \exp[-(k_{12} + k_{21})t])}{k_{12} + k_{21}} \\ \dfrac{k_{21}(1 - \exp[-(k_{12} + k_{21})t])}{k_{12} + k_{21}} & \dfrac{k_{12} + k_{21}\exp[-(k_{12} + k_{21})t]}{k_{12} + k_{21}} \end{pmatrix} \tag{11}$$

The transition probability matrix (11) corresponds to an operator $\hat{P}_t$. We will call operator $\hat{\hat{P}}_t$, which is the transpose of $\hat{P}_t$, the transition operator for the chemical system. It acts so as to transfer the system from one state on the PES tree to another [11].

The systems occupying some state E_i are characterized by their respective concentrations of the constituent substances, i.e. $C_A(t)$, $C_B(t)$, . . . etc. It seems natural to define the space in which acts the transition operator as the concentration-vector space. The concentration vector will be denoted by

$$|C_t(A, B, \ldots)\rangle = \begin{pmatrix} C_A(t) \\ C_B(t) \\ \ldots \\ \ldots \end{pmatrix}$$

The action of the transition operator $\hat{\hat{P}}_t$ on the concentration vector can be described by the relation [11]

$$\hat{\hat{P}}_t |C_0(A, B, \ldots)\rangle = |C_t(A, B, \ldots)\rangle \tag{12}$$

where $|C_0(A, B, \ldots)\rangle$ is the vector of original concentrations and $|C_t(A, B, \ldots)\rangle$ is the concentration vector at the moment t. Eq. (12) can be generalized in the following obvious way

$$\hat{\hat{P}}_\tau |C_\tau(A, B, \ldots)\rangle = |C_{t+\tau}(A, B, \ldots)\rangle \tag{13}$$

with $|C_\tau(A, B, \ldots)\rangle$ denoting a concentration vector at the moment τ.

Eqs. (12) and (13) are integral kinetic equations for the chemical system, presented in the matrix form. Thus, Eq. (12) for the first-order reversible reaction coincides with the integral equations of chemical kinetics obtained phenomenologically in [9]. If the original concentration vector (C_{A_0}, C_{B_0}) and the transition probabilities on the PES tree are known, then Eqs. (12) allow one to establish temporal dependence of the A and B concentrations.

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[2] A matrix whose elements are transition probabilities is called a Markov or stochastic matrix if the sum of elements in each row equals unity [8].

We have developed a kinetic model for the reaction that takes into account the PES properties and in a way can be regarded as an extension of the activated complex theory [1], allowing for concentration changes in the reactive system. The latter are described through PES parameters.

It should be noted that the Markovian nature of chemical reactions has been assumed here without the necessary foundations. In paper [13] an example has been presented of a non-Markovian chemical transformation, thus defining qualitatively the limits of validity for the Markov models. In particular, it has been shown that such reactions whose products serve as their own catalysers (auto-catalytic reactions) are non-Markovian.

6. Conclusions

The present investigations have shown that a complicated mathematical object which cannot be described visually, namely the multidimensional potential energy surface of a chemical reaction, can be substituted for many purposes with another object that is quite visual, i.e. the surface tree. The study of many properties of the function depending on many variables (like position of its stationary points) can be reduced to an investigation of a function of one argument. The latter is specified on the tree and has the value domain coincident with that of $U(q_1, \ldots, q_n)$. The PES tree provides a convenient model both for adiabatic and non-adiabatic reactions, which are useful for kinetic purposes in the case of multidimensional PES's. In contrast to the kinetic models known in the literature, the model suggested is based on the knowledge of topology of the PES stationary points distribution. The model allows one to determine the system component concentrations at any time moment from the knowledge of initial concentrations, provided transition probabilities are known in the space of potential energy stationary values.

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Received January 8, 1975/May 6, 1976