ADVANCES IN CHEMICAL PHYSICS

Volume IV

ADVANCES IN
CHEMICAL PHYSICS

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VOLUME IV

INTRODUCTION

In the last decades, chemical physics has attracted an ever increasing amount of interest. The variety of problems, such as those of chemical kinetics, molecular physics, molecular spectroscopy, transport processes, thermodynamics, the study of the state of matter, and the variety of experimental methods used, makes the great development of this field understandable. But the consequence of this breadth of subject matter has been the scattering of the relevant literature in a great number of publications.

Despite this variety and the implicit difficulty of exactly defining the topic of chemical physics, there are a certain number of basic problems that concern the properties of individual molecules and atoms as well as the behavior of statistical ensembles of molecules and atoms. This new series is devoted to this group of problems which are characteristic of modern chemical physics.

As a consequence of the enormous growth in the amount of information to be transmitted, the original papers, as published in the leading scientific journals, have of necessity been made as short as is compatible with a minimum of scientific clarity. They have, therefore, become increasingly difficult to follow for anyone who is not an expert in this specific field. In order to alleviate this situation, numerous publications have recently appeared which are devoted to review articles and which contain a more or less critical survey of the literature in a specific field.

An alternative way to improve the situation, however, is to ask an expert to write a comprehensive article in which he explains his view on a subject freely and without limitation of space. The emphasis in this case would be on the personal ideas of the author. This is the approach that has been attempted in this new series. We hope that as a consequence of this approach, the series may become especially stimulating for new research.

Finally, we hope that the style of this series will develop into something more personal and less academic than what has become the standard scientific style. Such a hope, however, is not likely to

be completely realized until a certain degree of maturity has been attained — a process which normally requires a few years.

At present, we intend to publish one volume a year, but this schedule may be revised in the future.

In order to proceed to a more effective coverage of the different aspects of chemical physics, it has seemed appropriate to form an editorial board. I want to express to them my thanks for their cooperation.

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RANDOM WALK AND RELATED PHYSICAL PROBLEMS*

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CONTENTS

I. INTRODUCTION

Differential equations, which relate the probabilities of locations of particles in a system with some prescribed initial probability distribution, can be expressed in two ways. One approach makes use of the continuum assumption, which leads to equations such as Fick's equation for diffusion. The other treats the system as a random-walk problem, which leads to a type of difference equation involving the transition probabilities of the particles. Generally the continuum approach fails to relate accurately the behavior of particles in terms of transition probabilities involved in the transport processes. It is, therefore, desirable to treat problems by the latter approach.

The "random-walk treatment" is especially necessary for describing consecutive reactions in chemical kinetics[8], the relaxation of a system of a harmonic oscillator[24] in a vibrational non-equilibrium

distribution, the probable nucleation mechanism in condensed systems,[35] some problems connected with diffusion processes,[41] and, in general, the study of non-equilibrium rate processes. Attempts to obtain the general solution of the difference equation starting from different assumptions has been made by various authors. Eyring and Zwolinski[10] used a model which describes qualitatively the deviation of the rate constant based on the "equilibrium viewpoint" from that based on the "non-equilibrium viewpoint." The model takes account of two energy levels for both reactants and products with arbitrarily assigned rate constants. The extension of this four-level approach to that of N-level approach was suggested by Shuler, Zwolinski, and Eyring[32] in describing microscopic non-equilibrium chemical kinetics. Montroll and Shuler[25] applied the "Pauli equation"[36] (a linear matrix difference equation involving the first-order derivatives of time) in order to extend the Zwolinski-Eyring model to more realistic problems; i. e., they treated the decomposition of diatomic molecules, by introducing the Landau-Teller[18] transition probabilities for the linear perturbation of diatomic molecules. In this case, the method of diagonalizing the matrix appearing in the transport equation is successful in a certain aspect, for the recursion formula of the Gottlieb polynomials[14] can be related to a set of recursion formulas for eigenvectors of the matrix having elements which are the Landau-Teller transition probabilities. The concentration change with respect to time in this case can be expressed as a linear combination of the Gottlieb polynomials. Further extension of this treatment in this direction has encountered the mathematical difficulty of solving the roots of the Gottlieb polynomial, $l_{N+1}(\mu) = 0$. Thus, only the asymptotic cases can be discussed satisfactorily. The extension along this line using a Morse harmonic oscillator with the nearest and the next nearest neighbor transition probabilities was discussed by Kim.[17]

Eyring and his associates apply similar difference equations to diffusion processes. In particular, Zwolinski, Eyring, and Reese[41] developed a theory for the diffusion in a steady state and for the permeability of membranes by considering molecular jumps from one equilibrium position to another. The theory was successfully applied to the permeability data of water, aliphatic alcohols, and

amides through animal and plant cells. Further theoretical consideration of the multi-barrier kinetics for diffusion processes was made by Parlin and Eyring,[30] and Giddings and Eyring.[13] The equations derived by these authors were, however, limited by the steady-state assumption and to nearest-neighbor transitions.

Any multi-barrier process (a random-walk problem) has a relaxation time associated with each microscopic jump. Thus, the steady-state approach fails to predict the transients during the initial period. The appearance of induction periods is frequently observed in chain reactions.[6] The induction period occurs also in the recrystallization of cold worked aluminum.[1] These induction periods are understandable in terms of the multi-barrier processes. Further interest in the random-walk treatment lies in the fact that time-dependence of concentration changes in various systems can be predicted.

By solving characteristic equations associated with the matrix occurring in the transport equation, we shall derive the general, non-steady-state solutions corresponding to several multi-barrier potential profiles which are physically important. The expression thus obtained will be used for calculating the mean first passage time of a particle in the random-walk process and the time-dependent concentration in a particular potential well.

II. RANDOM-WALK AND MULTI-BARRIER KINETICS

A fairly general transport equation for the random walk of particles with absorbing and reflecting barriers and with sources can be represented as follows:

$$\frac{dC_n}{dt} = \sum_{i=0}^{N} k_{ni} C_i - \sum_{j=0}^{N+1} k_{jn} C_n + \frac{d\varrho_n}{dt} \tag{1a}$$

$$= -\sum_{i=0}^{N} A_{ni} C_i + \frac{d\varrho_n}{dt} \tag{1b}$$

where

$$A_{ni} \equiv -k_{ni} + \left(\sum_{j=0}^{N+1} k_{ji} \right) \delta_{ni} \tag{2}$$

$$k_{ii} \equiv 0$$

Here k_{ni} denotes the transition probability (for convenience, the transition probability per unit time will be called just the transition probability) from the ith state to the nth; $C_n(t)$ is the concentration (or the probability for finding the particles when $C_n(t)$ is normalized) of the particles at the nth state at time t (see Figure 1); the first
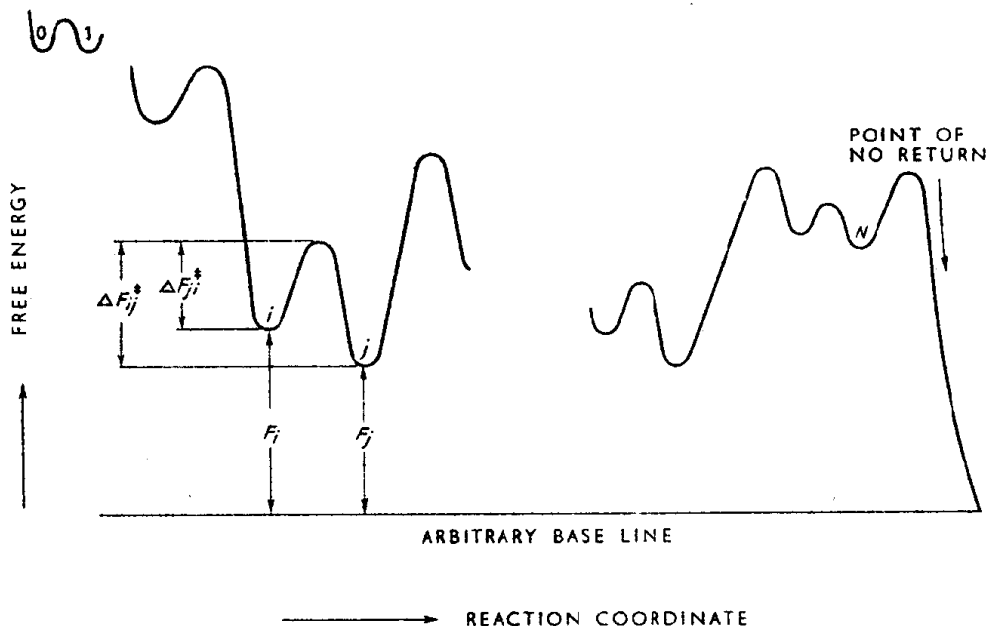
Fig. 1. Potential profile for an arbitrary multi-barrier system.

term on the right hand side of (1a) is the rate of increment of C_n, the second is the rate of decrement of C_n, and the last is the rate of production (or destruction) of C_n, if there exists an external source of the particles at the nth well. The assumptions involved in solving (1) will be stated next.

(i) It is assumed that no particle can jump backwards after it reaches the $(N+1)$th well; this assumption is taken to guarantee the positive definiteness of the matrix in (2). The proof for the positive definiteness is necessary to assure that the eigenvalues which appear in the exponents of the general solution of the differential equation (1) have positive values, and that the solutions obtained are not physically inconsistent. In a later section of this paper, a generalization to include any small perturbation in matrix A will

be given. Physically, the introduction of the point of no return, i. e., the $(N+1)$th well, is necessary to explain that a steady-state flux is achieved after an initial transient period. In the case when the potential profile extends to infinity, the introduction of the point of no return is automatically satisfied; and in the case where $k_{n, N+1}$ $(n = 0, 1, 2, \ldots)$ is small compared to other transition probabilities, the assumption of the zero backward-transition probabilities for the $(N+1)$th well is a very good approximation. For instance, in the diffusion of particles through a membrane, the backward-jump probability of a particle after it has completed travelling through the membrane will be negligible if the rate process under consideration is for passage through the membrane.

(ii) The transition probabilities are assumed to be independent of time and concentration. This assumption excludes applicability of the solution to the multi-barrier systems where the probabilities are dependent on time and concentration. However, fairly good approximate conclusions may be drawn from this approach to problems in which the transition probabilities are dependent on the variables concentration and time. The instances of transition probabilities independent of concentration and time occur in uni-molecular consecutive reactions in chemical kinetics, diffusion problems, transitions in vibrational levels of a diatomic molecule, and the cascading decays of nuclei such as the uranium-radium series $(4n+2)$. The effects of time and concentration on the transition probabilities can be treated by a perturbation method if necessary.

(iii) A microscopic reversibility between the ith and jth states is assumed. This approach is open to theoretical question; however all the empirical data agree with this assumption within the range of our interest. Chandrasekhar,[2] Montroll and Shuler,[25] and Kim[17] applied the principle of the microscopic reversibility to stochastic processes. The proof or disproof of the validity of the microscopic reversibility in actual rate processes has not yet been carried out successfully. The assumption of Onsager's reciprocal relation for transition probabilities[29] or the principle of detailed balance between two connecting states is another expression of this assumption.

Under assumption (iii),

$$K_{ij} \equiv (k_{ij}/k_{ji}) = e^{-(F_i - F_j)/RT}$$

where K_{ij} is the equilibrium constant between the ith and the jth potential wells. Then, we obtain the following relation

$$k_{ij}q_j = k_{ji}q_i \qquad q_i \equiv e^{(-F_i/RT)} \qquad (3)$$

In the case of diffusion, the reaction coordinate in Figure 1 represents the distance through which the particle must travel; if the unit processes are the consecutive reactions involving multi-barriers, the reaction coordinate represents the state of the system at a particular configuration and at a particular time. In describing multi-barrier kinetics, one should note that the free energy potential profiles have significance only at the minima and at the activated states. The shapes of the curves relating these maxima and minima do not play an important part in the cases here considered, since the entropy in the region connecting a minimum and an activated state is of no interest and is undefined.

The matrix A, Equation (2), has the following properties:

a. $\qquad A_{ij}q_j = A_{ji}q_i$ $\qquad\qquad\qquad\qquad\qquad\qquad$ (4)

b. $\qquad$ Positive eigenvalues $\qquad\qquad\qquad\qquad\qquad$ (5)

c. $\qquad \sum_{n=0}^{N} \psi_n^{(i)} q_n^{-1} \psi_n^{(j)} = \delta_{ij}; \quad \delta_{ij} = 1 \text{ if } i = j; \quad = 0 \text{ if } i \neq j$ (6)

as shown by other investigators.[17,25] Here $\psi^{(i)}$ is an eigenvector of A with eigenvalue λ_i, i. e.

$$A \psi^{(i)} = \lambda_i \psi^{(i)} \qquad (7)$$

In the case of the degeneracy, $\psi^{(i)}s$ can be properly orthogonalized to satisfy (6). Further, A has the following properties:

d. $\qquad \sum_{i=0}^{N} \psi_n^{(i)} q_n^{-1} \psi_k^{(i)} = \delta_{nk}$ $\qquad\qquad\qquad\qquad$ (8)

e. If the matrix contains only the nearest-neighbor transition probabilities, the corresponding eigenvectors and eigenvalues are related by the equation:

$$\sum_{n=0}^{N} q_r^{-1} \lambda_n^{-1} \psi_r^{(n)} \psi_N^{(n)} = (k_{N+1, N})^{-1}; \qquad r = 0, 1, 2, \ldots, N \qquad (9)$$

(cf. Appendix I).

Equation (8) follows from the following argument. Since A is a non-singular matrix of rank $N+1$, the square matrix P defined in (10a) also is of the $N+1$ rank; thus it has a unique inverse P^{-1} which satisfies the relation $P^{-1}P = PP^{-1} = I$. From Equations (6), (10a), and $P^{-1}P = I$, one obtains (10b). The substitutions of (10a) and (10b) into $PP^{-1} = I$ yields Equation (8).

$$\text{(a)} \quad (P_{ij}) = (\psi_i^{(j)}); \qquad \text{(b)} \quad (P_{ij}^{-1}) = (\psi_j^{(i)} q_j^{-1}) \qquad (10)$$

The transport equation (1) reduces to that proposed by Eyring and co-workers[41, 30, 13] at a steady state with only nearest-neighbor transition probabilities. By setting $\dot{\varrho}_n = \dot{\varrho}_0 \delta_{n0}$ and $dC_n(t)/dt = 0$ at the steady state, a transport equation of the following form is obtained from (1):

$$\left(\frac{\partial \varrho_0}{\partial t} \right)_{t \to \infty} \equiv Q \text{ (flux)} = k_{10} C_0 - k_{01} C_1 \qquad (11\,\text{a})$$

$$Q = k_{21} C_1 - k_{12} C_2 \qquad (11\,\text{b})$$

$$Q = ----\ --\ ----$$

$$Q = ----\ --\ ----$$

In general,

$$Q = k_{i+1, i} C_i - k_{i, i+1} C_{i+1} \quad (i = 0, 1, 2, \ldots, N-1) \quad (11\,\text{c})$$

and

$$Q = k_{N+1, N} C_N \qquad (11\,\text{d})$$

Equations (11a–d) are extensively applied by Eyring and his co-workers to the problems connected with steady states.

III. GENERAL SOLUTION OF THE TRANSPORT EQUATION

The $N + 1$ eigenvectors of the matrix A form a complete set,[17] and A has $N + 1$ positive eigenvalues, which forms a canonical matrix under similarity transformation, and is consequently non-singular. Thus, $C_k(t)$ and $\varrho_k(t)$ can be expanded as a linear combi-

nation of eigenvectors of the matrix A:

$$C_k(t) = \sum_{n=0}^{N} a_n(t)\psi_k^{(n)} \tag{12}$$

$$\varrho_k(t) = \sum_{n=0}^{N} b_n(t)\psi_k^{(n)} \tag{13}$$

Using the orthogonality condition (6) the quantity, $a_n(t)$, at $t = 0$ is determined by the initial distribution of $C_k(t)$; i. e.,

$$a_n(0) = \sum_{k=0}^{N} C_k(0)q_k^{-1}\psi_k^{(n)} \tag{14a}$$

$$b_n(0) = \sum_{k=0}^{N} \varrho_k(0)q_k^{-1}\psi_k^{(n)} \tag{14b}$$

Substituting (12) and (13) into (1b), and using the orthogonality relation (6), one obtains

$$\dot{a}_n(t) + \lambda_n a_n(t) = \sum_{i=0}^{N} \dot{\varrho}_i(t)q_i^{-1}\psi_i^{(n)} \tag{15}$$

the solution of which is given by

$$a_n(t) = e^{-\lambda_n t}\left[\int_0^t \sum_{i=0}^{N} \dot{\varrho}_i(t)q_i^{-1}\psi_i^{(n)} e^{\lambda_n t}\, dt + a_n(0)\right] \tag{16}$$

From (12) and (16), one obtains the general solution of (1):

$$C_k(t) = \sum_{n=0}^{N} e^{-\lambda_n t}\left(\int_0^t \sum_{i=0}^{N} \dot{\varrho}_i(t)q_i^{-1}\psi_i^{(n)} e^{\lambda_n t}\, dt + \sum_{i=0}^{N} C_i(0)q_i^{-1}\psi_i^{(n)}\right)\psi_k^{(n)} \tag{17}$$

IV. EIGENVALUES AND EIGENVECTORS OF MATRIX A

One can, therefore, solve the time-dependent random-walk problems if the transition probabilities for every possible configuration are known. As long as N is not large, the eigenvectors are, therefore, obtainable by using electronic computors. However, the particular solutions with *a priori* transition probabilities for large N are not, in general, obtainable.

We shall present here some potential profiles which give analytic expressions of ψ's and λ's for any N, and shall generalize these results to include broader multi-barrier problems. Nearest-neighbor transition probabilities only are involved throughout the following considerations except for the perturbation theory treatment; the inclusion of the next-nearest neighbor may be introduced by the perturbation method as discussed later.

A. A Potential Profile with Equal Forward-Nearest-Neighbor and Equal Backward-Nearest-Neighbor Transition Probabilities

Let all the forward transition probabilities be equal to b, i. e., $k_{i+1, i} = b$ $(i = 0, 1, \ldots, N)$, and let all the backward transition probabilities be equal to a; i. e., $k_{i-1, i} = a$ $(i = 1, \ldots, N)$. The representation is given in Figure 2B. Then the eigenvalues are the solution of the polynomial in λ of $|A - \lambda I| = 0$.

$$
|A - \lambda I| = \begin{vmatrix}
b - \lambda & -a & & & & 0 \\
-b & a + b - \lambda & -a & & & \\
& -b & a + b - \lambda & -a & & \\
& & - & - & - & \\
0 & & & & & -a \\
& & & & -b & a + b - \lambda
\end{vmatrix} \tag{18}
$$
$$
\longleftarrow \text{———} N + 1 \text{———} \longrightarrow
$$

$$
\equiv a^{N+1} \mathscr{D}_{N+1}(x) = 0
$$

where

$$
x \equiv 1 + (b/a) - (\lambda/a) \equiv 1 + c - (\lambda/a) \tag{19}
$$

$$
\mathscr{D}_{N+1}(x) \equiv \begin{vmatrix}
x - 1 & -1 & & & 0 \\
-c & x & -1 & & \\
& -c & x & -1 & \\
& & - & - & - \\
0 & & & & -1 \\
& & & -c & x
\end{vmatrix} \tag{20}
$$
$$
\longleftarrow \text{———} N + 1 \text{———} \longrightarrow
$$