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Theory of Rate Constants: Master Equation Approach

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Starting from the master equations we derive the kinetic equations for the concentrations of chemical species. Both adiabatic and nonadiabatic rate processes are analyzed. In limiting cases, the results of the work conform to those of Widom(9) and Gibbs, Fleming, and co-workers.(4,5)

KEY WORDS: Master equations; rate constants; transition states; adiabatic transitions; nonadiabatic transitions; Arrhenius law; transitions probabilities.

1. INTRODUCTION

One cannot overestimate the importance of the theory of rate processes in diverse areas of chemical physics and biophysics; nevertheless, our understanding of the theoretical basis of many rate processes is not complete even now. This is true both of the equations themselves and of their coefficients—the rate constants.

The problem of rate processes may be approached at various levels. The "upper" level is the derivation of rate equations and their coefficients from first principles, i.e., from the von Neumann equation for the density matrix of a closed system.

In the typical situation it is possible to divide the whole system into two parts. One part contains the subsystem we are interested in, e.g., the reacting molecules in the case of chemical reactions; the other part contains the surroundings: gaseous or condensed media. Under certain assumptions the von Neumann equation may be approximately reduced to the irrevers-

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ible master equations. There exists extensive literature devoted to this subject.(1) In Ref. 2, by the present author, special attention was devoted to the conditions of the derivation of a master equation for the subsystem we are interested in.

Of course, master equations may serve to describe various rate processes including the kinetics of chemical reactions, but a conventional and a simplified description of rate processes is based on the rate equations for total concentrations of various species.

The purpose of this work is to analyze the conditions under which the equations for total concentrations (disregarding the distribution over the microstates) may be derived from the master equations. Another aim is to express the rate constants in terms of the transition rates of the master equations. This is the level which will be considered in this paper.

The most popular theory of rate constants is the so-called transition state theory (TST).(3) This theory gives a very general expression for the reaction rates in terms of thermodynamic quantities of initial and transition states. Though this theory became the basic tool for processing the experimental data, the theoretical basis of it is not very clear and is still a subject for discussion. Connection of TST with master equations is also not clear.

On the other hand the stochastic theory of rate constants developed by Gibbs, Fleming, and co-workers(4, 5) exhibits clear linkage with master equations and it expresses the reaction rate constants in terms of the transition rates in master equations. The specific feature of this theory is that its validity is based on properties of solutions of master equations, rather than on relations among parameters of master equations.

To avoid the danger of not very clearly defined assumptions, specific models of chemical reactions were investigated. In 1940 Kramers(6) considered the model of particles in the double well potential. The Fokker–Planck equation was used to analyze this model and to check the accuracy of TST.

More recently, Montroll and Shuler,(7) Snider,(8) and Widom(9) considered quantum mechanical models of chemical reactions. They found rigorous asymptotically exact solutions of the master equations for their specific models.

Thus the situation may be described as follows. On the one hand we have expressions for the reaction rates stemming from a fairly general framework, but with ill-defined assumptions, and on the other hand we have rigorous solutions valid for very specific models.

We are going to bridge these alternative approaches. We start from general master equations and proceed to find rigorous restrictions imposed on the parameters of the master equations in order to derive expressions for the reaction rates in the equations for concentrations.

In Section 2 we consider a general model describing so-called adiabatic rate processes.

Section 3 is devoted to nonadiabatic rate processes.

In Section 4 we compare results of the work with the above-mentioned rigorous solutions(9) and make some concluding remarks.

2. ADIABATIC RATE PROCESSES

We will discuss the rate processes in condensed media,(10, 2) in solutions, solids, or in huge molecules, but as will be seen from the following, the results have more general meaning.

We divide the whole system into two subsystems: the system we are interested in, e.g., the molecules undergoing chemical transitions, and its surroundings: a condensed medium. In general one can regard the chemical transformations (as well as other rate processes) as transitions from one quasistable configuration of nuclei to another. In the framework of the Born–Oppenheimer approximation such transitions may occur either at one and the same electronic state or between various electronic states. The former transitions are called the adiabatic transitions and the latter nonadiabatic ones.

First we will consider the theory of adiabatic rate processes. That means that we will specify the subsystem under study by a single potential energy hypersurface with two potential wells divided by the barrier (Fig. 1).

Then, if the interaction of the subsystem with the surrounding medium is weak enough (and other conditions are fulfilled(2)) it is possible to derive the master equations for the subsystem

$$\frac{dP_n}{dt} = -\sum (w_{nk}P_n - w_{kn}P_k) \tag{1}$$

Here P_n is the probability of the microstate n, and w_{nk} is the rate of transition between states n and k.

We will assume that the temperature of the surrounding medium is large enough so that transitions between wells are mainly due to thermal fluctuations induced by the medium and the tunneling may be neglected. In particular, this may mean that the temperature is larger than characteristic energy difference $\hbar\omega_0$ between adjacent levels:

$$k_B T \gg \hbar\omega_0 \tag{2}$$

At the same time we consider the temperature region

$$k_B T \ll U_a \tag{3}$$

where U_a is the characteristic height of a barrier between two wells. (In the

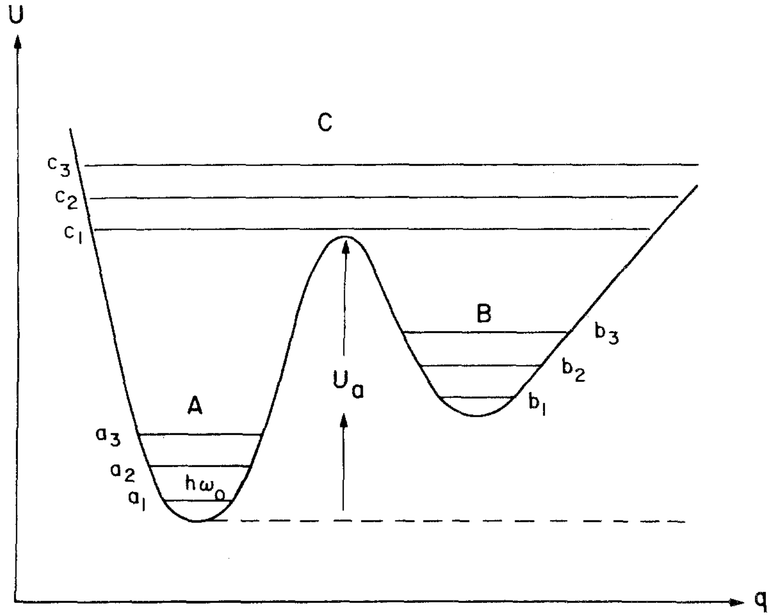

Fig. 1. The potential energy curve represents a hypersurface with two potential wells. a_i, microstates of A species; b_i, microstates of B species; c_i, microstate of a transition state C.

opposite case $k_BT \gtrsim U_a$ one cannot specify well-localized species in wells A and B.)

Though the following analysis has a more general meaning, we have in mind some reaction of isomerization (or transfer of a molecular group from site A to site B). We define three types of states a, b, and c (Fig. 1). States a characterize the isomer A, states b characterize the isomer B, and the states c characterize some transition state C.

Neglecting tunneling, the transition from the states a to the states b, i.e., the reaction

$$A \rightleftarrows B \tag{4}$$

may proceed only through the transition state C. In other words, the only transitions we take into account are those between a, b, c, themselves, and those between a, and c, b and c. Thus, we take into account the following transition probabilities:

$$w_{aa'}, \quad w_{bb'}, \quad w_{cc'} \text{ and } w_{ca}, \quad w_{cb}, \quad w_{ac}, \quad w_{bc}$$

The corresponding master equations describing the reaction (4) may be written in the form

$$\dot{P}_a = -\sum_{a'}(w_{aa'}P_a - w_{a'a}P_{a'}) + \sum_{c}(w_{ca}P_c - w_{ac}P_a) \tag{5}$$

$$\dot{P}_b = -\sum_{b'}(w_{bb'}P_b - w_{b'b}P_{b'}) + \sum_{c}(w_{cb}P_b - w_{bc}P_b) \tag{6}$$

$$\begin{aligned}\dot{P}_c = {} & \sum_{a}(w_{ac}P_a - w_{ca}P_c) + \sum_{b}(w_{bc}P_b - w_{cb}P_c) \\ & + \sum_{c'}(w_{cc'}P_c - w_{c'c}P_{c'})\end{aligned} \tag{7}$$

As is known, for the equilibrium surrounding medium, the transition probabilities w_{ab} satisfy the relation

$$w_{ab} = w_{ba}\exp\left[\,\beta(E_a - E_b)\right] \tag{8}$$

where E_a is the energy of the microstate a and

$$\beta = 1/k_B T$$

In general, one can look for the solutions of Eqs. (5)–(7) in the form of the quasiequilibrium expressions

$$C_A(t)e^{-\beta E_a}/\Sigma_A, \qquad C_B(t)e^{-\beta E_b}/\Sigma_B$$

corresponding to the site A and B plus the correction terms η_a and η_b, respectively. It will be shown later on that these correction terms are small provided conditions (3) and (20) are satisfied.

Thus we write

$$\begin{aligned} P_a &= C_A(t)\left(e^{-\beta E_a}/\Sigma_A\right) + \eta_a \\ P_b &= C_B(t)\left(e^{-\beta E_b}/\Sigma_B\right) + \eta_b \\ P_c &= N_c e^{-\beta E_c} \end{aligned} \tag{9}$$

where

$$\Sigma_A = \sum_a e^{-\beta E_a}, \qquad \Sigma_B = \sum_b e^{-\beta E_b} \tag{10}$$

are the statistical sums of the states A and B; C_A and C_B are total concentrations of the species A and B, respectively,

$$C_A = \sum_a P_a, \qquad C_B = \sum_b P_b \tag{11}$$

The quantities η_a and η_b satisfy the normalization conditions

$$\sum_a \eta_a = \sum_b \eta_b = 0 \tag{12}$$

Substituting (9) into (5)–(7) and using (8), we get

$$\dot{\eta}_a = \sum_{a'} (w_{a'a}\eta_{a'} - w_{aa'}\eta_a) - \sum_c w_{ca}\eta_a e^{\beta(E_a - E_c)}$$
$$+ \sum_c w_{ca} N_c e^{-\beta E_c} - \sum_c w_{ca}\left(e^{-\beta E_c}/\Sigma_A\right) C_A - C'_A\left(e^{-\beta E_a}/\Sigma_A\right) \qquad (13)$$

$$\dot{\eta}_b = \sum_{b'} (w_{b'b}\eta_{b'} - w_{bb'}\eta_b) - \sum_b w_{cb}\eta_b e^{\beta(E_b - E_c)}$$
$$+ \sum_c w_{cb} N_c e^{-\beta E_c} - \sum_c w_{cb} C_B\left(e^{-\beta E_c}/\Sigma_B\right) - C'_B\left(e^{-\beta E_b}/\Sigma_B\right) \qquad (14)$$

$$\dot{N}_C = (\gamma_{cA} C_A/\Sigma_A) + (\gamma_{cB} C_B/\Sigma_B) - (\gamma_{cA} + \gamma_{cB}) N_c$$
$$- \sum_{c'} w_{cc'}(N_c - N_{c'}) + \sum_a w_{ca}\eta_a e^{\beta(E_a - E_c)}$$
$$+ \sum_b w_{cb}\eta_b e^{\beta(E_b - E_c)} \qquad (15)$$

Here

$$\gamma_{cA} = \sum_a w_{ca}, \qquad \gamma_{cB} = \sum_b w_{cb} \qquad (16)$$

Performing summation over a and b in (13) and (14) we get

$$\dot{C}_A = \sum_c e^{-\beta E_c}\gamma_{cA}(N_c - (C_A/\Sigma_A)) - \sum_{ca} w_{ca}\eta_a e^{-\beta(E_c - E_a)} \qquad (17)$$

$$\dot{C}_B = \sum_c e^{-\beta E_c}\gamma_{cB}(N_c - (C_B/\Sigma_B)) - \sum_{cb} w_{cb}\eta_b e^{-\beta(E_c - E_b)} \qquad (18)$$

When condition (3) is satisfied it is easy to verify from (13) and (14) that η_a, η_b have the order of the magnitude

$$\eta_a \sim C_A\left(e^{-\beta E_c}/\Sigma_A\right), \qquad \eta_b \sim C_B\left(e^{-\beta E_c}/\Sigma_B\right) \qquad (19)$$

Using these estimates one can simplify equations (15), (17), (18) and omit terms containing η_a, η_b, provided the following conditions are fulfilled:

$$\frac{\sum_a w_{ca} e^{-\beta(E_c - E_a)}}{\sum_a w_{ca}} \ll 1$$
$$\frac{\sum_b w_{cb} e^{-\beta(E_c - E_b)}}{\sum_b w_{cb}} \ll 1 \qquad (20)$$

In this case the equations (15), (17), (18) obtain the form

$$\dot{N}_c = (\gamma_{cA}/\Sigma_A)C_A + (\gamma_{cB}/\Sigma_B)C_B - (\gamma_{cA} + \gamma_{cB})N_c - \sum_{c'} w_{cc'}(N_c - N_{c'}) \tag{21}$$

$$\dot{C}_A = \sum_c e^{-\beta E_c}\gamma_{cA}(N_c - (C_A/\Sigma_A)) \tag{22}$$

$$\dot{C}_B = \sum_c e^{-\beta E_c}\gamma_{cB}(N_c - (C_B/\Sigma_B)) \tag{23}$$

Examining these equations, one realizes that the concentrations C_A and C_B are slow variables in comparison with N_c. The derivatives $\dot{C}_A$ and $\dot{C}_B$ contain the extra factor of the order of magnitude $\exp(-\beta U_a)$ which $\dot{N}_c$ do not contain. It means that in the same approximation (3) one can use the steady state condition

$$\dot{N}_c = 0$$

Thus we have from (21)

$$N_c = \frac{1}{\gamma_{cA} + \gamma_{cB}}\left(\frac{\gamma_{cA}}{\Sigma_A}C_A + \frac{\gamma_{cB}}{\Sigma_B}C_B\right) + \frac{1}{\gamma_{cA} + \gamma_{cB}}\sum_{c'} w_{cc'}(N_c - N_{c'}) \tag{24}$$

The equations (22)–(24) solve the problem of time evolution of the total concentrations C_A, C_B in the course of the reaction.[11]

In various limiting cases they may be essentially simplified. The equation (24) has the exact solution in the case of symmetric wells, when

$$\Sigma_A = \Sigma_B = \Sigma, \qquad \gamma_{cA} = \gamma_{cB} = \gamma_c$$

and

$$N_c = \frac{1}{2\Sigma}(C_A + C_B)$$

The equations (22), (23) for the concentrations obtain the form

$$\dot{C}_A = -k(C_A - C_B) = -\dot{C}_B \tag{25}$$

where the reaction rate constant k has the form

$$k = \frac{\sum_c \gamma_c e^{-\beta E_c}}{2\Sigma} = \frac{1}{2}\bar{\gamma}e^{-\beta(F_C - F_A)} \tag{26}$$

Here the mean value of the transition probability equals

$$\bar{\gamma} = \frac{\sum_c \gamma_c e^{-\beta E_c}}{\sum_c e^{-\beta E_c}} \tag{27}$$

and the free energies of the initial state F_A ($= F_B$) and the transition state

F_C are expressed through the statistical sums in the usual way:

$$e^{-\beta F_A} = \sum_a e^{-\beta E_a}, \qquad e^{-\beta F_C} = \sum_c e^{-\beta E_c} \tag{28}$$

The equations (22)–(24) may also be simplified in two limiting cases:

(a) The relaxation between microstates c of the transition state C is much slower than relaxation from the state c to the states a and b:

$$\gamma_{cA}, \gamma_{cB} \gg w_{cc'} \tag{29}$$

In this case the approximate solution of (24) takes the form

$$N_c = \frac{1}{\gamma_{cA} + \gamma_{cB}} \left(\frac{\gamma_{cA}}{\Sigma_A} C_A + \frac{\gamma_{cB}}{\Sigma_B} C_B \right) \tag{30}$$

and the equations for the concentrations C_A and C_B obtain the form

$$\dot{C}_A = -k_{AB} C_A + k_{BA} C_B = -\dot{C}_B \tag{31}$$

where

$$\begin{aligned} k_{AB} &= \gamma_{ACB} e^{-\beta(F_C - F_A)} \\ k_{BA} &= \gamma_{ACB} e^{-\beta(F_C - F_B)} \end{aligned} \tag{32}$$

Here, again, F_C is the free energy of the transition state, and F_A, F_B are those of the states A and B. The preexponential factor in (32) is defined by the formula

$$\gamma_{ACB} = \frac{1}{\sum_c e^{-\beta E_c}} \sum_c \frac{\gamma_{cA} \gamma_{cB}}{\gamma_{cA} + \gamma_{cB}} e^{-\beta E_c} \tag{33}$$

It is easy to verify that the ratio of the rate constants (32) is equal to the equilibrium constant

$$\left(\frac{C_A}{C_B} \right)_{t \to \infty} = K = \frac{k_{BA}}{k_{AB}} = e^{-\beta(F_A - F_B)} \tag{34}$$

as it should be.

(b) The relaxation between the microstates c of the transition state C is much faster than relaxation from the transition microstate c to the states a and b:

$$\gamma_{cA}, \gamma_{cB} \ll w_{cc'} \tag{35}$$

To analyze this case we will express N_c through P_c [see (9)] and rewrite (24) in the form

$$(\gamma_{cA} + \gamma_{cB}) P_c + \sum_{c'} (w_{cc'} P_c - w_{c'c} P_c) = \left(\frac{\gamma_{cA}}{\Sigma_A} + \frac{\gamma_{cB}}{\Sigma_B} \right) e^{-\beta E_c} \tag{36}$$

Performing summation over c in this formula we get

$$\sum_c (\gamma_{cA} + \gamma_{cB}) P_c = \sum_c \left(\frac{\gamma_{cA}}{\Sigma_A} C_A + \frac{\gamma_{cB}}{\Sigma_B} C_B \right) e^{-\beta E_c} \tag{37}$$

One can check from (36) that neglecting terms of the order of magnitude $\gamma_{cA}/w_{cc'}, \gamma_{cB}/w_{cc'}$ [they are small according to the condition (35)] it is possible to present P_c as

$$P_c = \frac{c_0}{\Sigma_C} e^{-\beta E_c} \equiv N_c e^{-\beta E_c} \tag{38}$$

where c_0 is found by substituting (38) for (37):

$$c_0 = \frac{\Sigma_0}{\gamma_{CA} + \gamma_{CB}} \left(\frac{\gamma_{CA}}{\Sigma_A} C_A + \frac{\gamma_{CB}}{\Sigma_B} C_B \right) \tag{39}$$

Here

$$\gamma_{CA} = \frac{\sum_c \gamma_{cA} e^{-\beta E_c}}{\sum_c e^{-\beta E_c}}, \qquad \gamma_{CB} = \frac{\sum_c \gamma_{cB} e^{-\beta E_c}}{\sum_c e^{-\beta E_c}} \tag{40}$$

Substituting expressions for N_c from (38), (39) for (22), (23) we again get the rate equation (31) with the rate constants equal

$$\begin{aligned} k_{AB} &= \frac{\gamma_{CA}\gamma_{CB}}{\gamma_{CA} + \gamma_{CB}} e^{-\beta(F_C - F_A)} \\ k_{BA} &= \frac{\gamma_{CA}\gamma_{CB}}{\gamma_{CA} + \gamma_{CB}} e^{-\beta(F_C - F_B)} \end{aligned} \tag{41}$$

The expressions (40), (41) coincide with those found by Gibbs, Fleming and co-workers.[4, 5] As we see, their expressions are obtained as a specific case from the general formalism. Of course the expressions (41) satisfy the relation (34).

3. NONADIABATIC RATE PROCESSES

Another possible class of rate processes are the so-called nonadiabatic transitions. In this case each of species A and B has its own corresponding potential energy—electronic energy as a function of the coordinates of nuclei. The minimum of each potential energy hypersurface corresponds to (quasi) stable configuration of nuclei. We assume that these potential energy hypersurfaces are intersecting ones (Fig. 2). The experience of the theory of Landau–Zener transitions[12] teaches us that at high enough temperatures (neglecting tunneling) the effective transitions are between microstates a and b (of A and B) which lie above the intersection point of minimal energy.

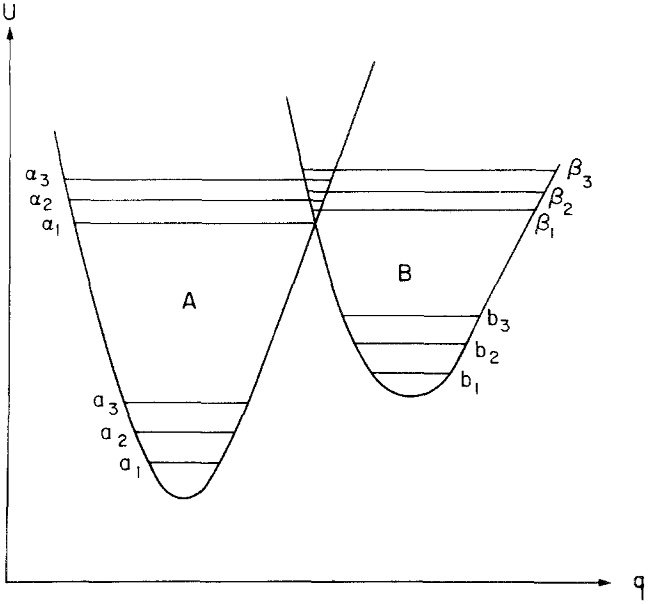

Fig. 2. Two intersecting potential energy curves represent two intersecting potential energy hypersurfaces. a_i, b_i, microstates lying below the intersection point with minimal energy; α_j, β_j, microstates lying above the intersection point.

Thus we introduce two kinds of microstates A: a and α, and two kinds of microstates B: b and β. Microstates α and β lie above the point of intersection of minimal energy. The transition probabilities between these states are assumed to be much larger than those among states a and b (the latter corresponds to the tunneling).

The corresponding master equations take the form

$$\dot{P}_a = -\sum_{a'}(w_{aa'}P_a - w_{a'a}P_{a'}) - \sum_{\alpha}(w_{a\alpha}P_a - w_{\alpha a}P_\alpha) \tag{42}$$

$$\dot{P}_b = -\sum_{b'}(w_{bb'}P_b - w_{b'b}P_{'}) - \sum_{\beta}(w_{b\beta}P_b - w_{\beta b}P_\beta) \tag{43}$$

$$\dot{P}_\alpha = -\sum_{a}(w_{\alpha a}P_\alpha - w_{a\alpha}P_a) - \sum_{\beta}(w_{\alpha\beta}P_\alpha - w_{\beta\alpha}P_\beta)$$
$$-\sum_{\alpha'}(w_{\alpha\alpha'}P_\alpha - w_{\alpha'\alpha}P_{\alpha'}) \tag{44}$$

$$\dot{P}_\beta = -\sum_{\beta}(w_{\beta b}P_\beta - w_{b\beta}P_b) - \sum_{\alpha}(w_{\beta\alpha}P_\beta - w_{\alpha\beta}P_\alpha)$$
$$-\sum_{\beta'}(w_{\beta\beta'}P_\beta - w_{\beta'\beta}P_{\beta'}) \tag{45}$$

First, let us consider the case when the transition probabilities between different electronic states are much smaller than those among different levels in the same state A or B

$$w_{\alpha\beta} \ll w_{aa'}, w_{\alpha\alpha'}, w_{\alpha a}, w_{bb'}, \ldots \tag{46}$$

In this case the probability distribution of microstates of state A or B may be approximated by the expressions

$$\begin{aligned} P_a &= C_A(t)\frac{e^{-\beta E_a}}{\Sigma_A} + O\left(\frac{w_{\alpha\beta}}{w_{aa'}}, \cdots\right) \\ P_\alpha &= C_A(t)\frac{e^{-\beta E_\alpha}}{\Sigma_A} + O\left(\frac{w_{\alpha\beta}}{w_{\alpha\alpha'}}, \cdots\right), \qquad \text{etc.} \end{aligned} \tag{47}$$

where

$$\Sigma_A = \sum_a e^{-\beta E_a} + \sum_\alpha e^{-\beta E_\alpha} \tag{48}$$

Here we neglect corrections of the thermodynamic equilibrium in each state of A and B. These corrections are small due to the condition (46).

Substituting expressions (47) (without small corrections) for the master equations (41)–(44) we get the rate equations for the overall concentrations C_A and C_B of species A and B

$$\dot{C}_A = -k_{AB}C_A + k_{BA}C_B \tag{49}$$

where the rate constants are equal to

$$k_{AB} = \frac{\sum_{\alpha\beta} w_{\alpha\beta} e^{-\beta E_\alpha}}{\Sigma_A}, \qquad k_{BA} = \frac{\sum_{\alpha\beta} w_{\beta\alpha} e^{-\beta E_\beta}}{\Sigma_B} \tag{50}$$

These expressions are also valid in the case when α, β take all the meanings, including a and b. It means that they may also take into account tunneling between the microstates of A and B. These expressions may be used at all temperatures.

In the case of high temperatures when the tunneling may be neglected and the temperatures simultaneously satisfying the condition (3), the expression may be approximately rewritten in the form explicitly exhibiting the Arrhenius law

$$k_{AB} = we^{-\beta(\tilde{F}_A - F_A)}, \qquad k_{BA} = we^{-\beta(\tilde{F}_B - F_B)} \tag{51}$$

where

$$w = \frac{\sum_{\alpha\beta} w_{\alpha\beta} e^{-\beta E_\alpha}}{\sum_\alpha e^{-\beta E_\alpha}} \tag{52}$$

$$e^{-\beta\tilde{F}_A} = \sum_\alpha e^{-\beta E_\alpha}, \qquad e^{-\beta F_A} = \sum_a e^{-\beta E_a} \tag{53}$$

It is easy to check that the thermodynamic equilibrium relation (34) is satisfied by the expressions (50)–(53).

Now, let us consider the case opposite to (46), i.e., the case

$$w_{\alpha\beta} \gg w_{\alpha\alpha'}, w_{\beta\beta'} \tag{54}$$

We assume that the condition (3) is satisfied.

This case may be analyzed similarly to case (35) of adiabatic transitions. The resulting rate constants have the form

$$\begin{aligned} k_{AB} &= \frac{\gamma_A \gamma_B}{\gamma_A + \gamma_B} e^{-\beta(F_0 - F_A)} \\ k_{BA} &= \frac{\gamma_A \gamma_B}{\gamma_A + \gamma_B} e^{-\beta(F_0 - F_B)} \end{aligned} \tag{55}$$

where the free energy of the "activated complex" (of the "transition state") is defined as

$$e^{-\beta F_0} = \sum_\alpha e^{-\beta E_\alpha} + \sum_\beta e^{-\beta E_\beta} = \Sigma_0 \tag{56}$$

and

$$e^{-\beta F_A} = \sum_a e^{-\beta E_a}, \qquad e^{-\beta F_B} = \sum_b e^{-\beta E_b} \tag{57}$$

The constants γ_A, γ_B are defined as

$$\gamma_A = \frac{\sum_{\alpha a} w_{\alpha a} e^{-\beta E_\alpha}}{\Sigma_0}, \qquad \gamma_B = \frac{\sum_{\beta b} w_{\beta b} e^{-\beta E_\beta}}{\Sigma_0} \tag{58}$$

As can be seen from the comparison of formulas (41) and (55), the nonadiabatic transitions in the case (54) exhibit a very close similarity to the adiabatic transitions. In this case the reaction rates k_{AB}, k_{BA} are determined not by transition probabilities $w_{\alpha\beta}$ between states A and B, but by the relaxation rates $w_{\alpha a}, w_{\beta b}$ between various microstates at the same electronic hypersurfaces A or B.

4. CONCLUDING REMARKS

To gain better insight into the essence of the expressions obtained for the reaction rates, it is instructive to compare them with rigorous asymptotically exact expressions of Widom.(9) For this purpose we recall Widom's results and identify them in terms of the present work. In Fig. 3 the stepladder model of Widom and connection with our designations are shown. Widom's formulas are valid for fixed

$$\alpha = e^{-\beta\epsilon}$$

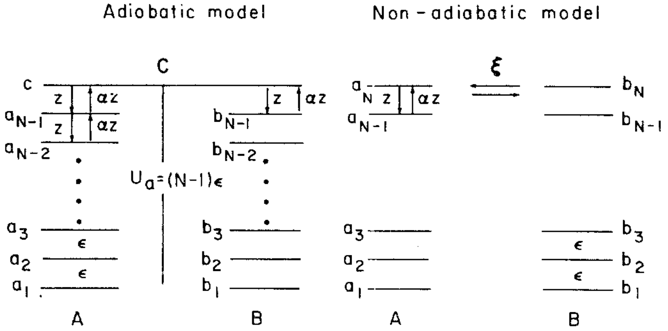

Fig. 3. Stepladder model of Widom.[9] ϵ, energy difference between the adjacent levels; $z = w_{aa'} = w_{bb'}$, downwards transition probabilities; $\alpha z = w_{a'a} = w_{b'b}$, upwards transition probabilities; $W_{ca} = W_{cb} = z = W_{ac}/\alpha = W_{bc}/\alpha$, transition probabilities between transition state C and state a and b in the adiabatic model; $W_{a_N b_N} = W_{b_N a_N} = \zeta$ transition probabilities between states A and B in the nonadiabatic model.

and $N \to \infty$, where the activation energy is equal

$$U_a = (N-1)\epsilon$$

The quantity ϵ is the energy difference between the adjacent levels (the energy spectrum is equidistant). It is clear that condition $N \to \infty$ corresponds to our condition (3), since

$$U_a/k_B T = -(N-1)\ln\alpha \gg 1$$

and

$$\alpha^{N-1} = e^{-\beta U_a} \tag{59}$$

In Table I we compare the corresponding formulas of Widom with ours. (These formulas are valid for the symmetric case.)

We see that the formulas of the present work and those of Widom

Table I

Reaction rates	
Widom's paper[9]	Present work
Adiabatic transitions	
$k_{AB} = k_{BA} = \frac{1}{2}z(1-\alpha)^2 e^{-\beta U_a}$	$k_{AB} = k_{BA} = \frac{1}{2}z(1-\alpha)e^{-\beta U_a}$
Nonadiabatic transitions	
$k_{AB} = k_{BA} = \dfrac{(1-\alpha)^2}{[(1-\alpha)/\zeta] + 2/z}$	$k_{AB} = k_{BA} = \dfrac{z(1-\alpha)\zeta}{z+2\zeta}e^{-\beta U_a}$

coincide, provided

$$\alpha \ll 1$$

This condition coincides with that of (20) which for the stepladder model has the form

$$\frac{\sum_a w_{ca} e^{-\beta(E_c - E_a)}}{\sum w_{ca}} = \frac{ze^{-\beta\epsilon}}{z} = \alpha \ll 1 \qquad (60)$$

Another instance when the formula of the present work coincides with that of Widom is the case of small nonadiabatic transitions (46) which corresponds to

$$\zeta \ll z$$

In this case our formulas coincide with those of Widom, not dependent upon the fulfillment of condition (60). [Of course the condition (60) is not very realistic since it means

$$k_B T \ll \epsilon$$

In this case the tunneling may play an important role. In Widom's model this possibility is excluded.]

In general, the condition (20) may be rewritten in the form

$$\frac{\bar{w}_{cA}}{\tilde{w}_{cA}} \frac{\sum_a e^{-\beta(E_c - E_a)}}{N} \ll 1 \qquad (E_c \geqslant E_a) \qquad (61)$$

where

$$\bar{w}_{cA} = \frac{\sum_a w_A e^{-\beta(E_c - E_a)}}{\sum_a e^{-\beta(E_c - E_a)}} \qquad \tilde{w}_{cA} = \frac{\sum_a w_{ca}}{N}$$

and N is the total number of the states a. When $\bar{w}_{cA}$ and $\tilde{w}_{cA}$ are of the same order of magnitude (this is not the case in the Widom model) the conditions (61) [and (20)] are satisfied.

Connection with the transition state theory (TST) should be remarked upon. The starting point of our consideration was the use of the master equations. This implies that the transition probabilities determining the reaction rates are much smaller than the characteristic frequencies of the unperturbed motion. On the other hand, in TST the reaction rates are determined by the characteristic frequency of unperturbed motion $k_B T/\hbar$. Thus we cannot compare our formulas with those of TST. Our results conform to the analysis of Kramers [6] according to which the reaction rate is proportional to the viscosity η (and not to $k_B T/\hbar$) for the case of small viscosities.

In conclusion, we again stress that the main result of the present work is the consistent derivation of the rate equations for the macroscopic concentrations from the master equations describing the evolution of the microstates. Both adiabatic and nonadiabatic transitions were considered and various specific cases were analyzed.

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REFERENCES

1. I. Oppenheimer, K. E. Shuler, G. H. Weiss, *Stochastic Processes in Chemical Physics: The Master Equation* (MIT Press, Cambridge, Massachusetts, 1977).
2. B. Fain, *Physica* **101A**:67 (1980).
3. S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill, New York, 1941).
4. J. H. Gibbs, *J. Chem. Phys.* **57**:4473 (1972).
5. J. H. Gibbs and P. D. Fleming III, *J. Stat. Phys.* **12**:375 (1975); A. M. Dunker, J. E. Lusk, and J. H. Gibbs, *Biophys. Chem.* **11**:9 (1980).
6. H. A. Kramers, *Physica* 7:284 (1940).
7. E. W. Montroll and K. E. Shuler, *Adv. Chem. Phys.* **1**:361 (1958).
8. N. S. Snider, *J. Chem. Phys.* **42**:548 (1965).
9. B. Widom, *J. Chem. Phys.* **55**:44 (1971).
10. B. Fain, *Phys. Stat. Sol.* (*b*) **63**:411 (1974); *Chem. Phys. Lett.* **56**:503 (1978); *Theory of Rate Processes in Condensed Media* (Springer-Verlag, Berlin, 1980).
11. B. Fain, *Chem. Phys. Lett.* **67**:267 (1979).
12. L. Landau and E. Lifshitz, *Quantum Mechanics* (Pergamon Press, London, 1958).