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The influence of the "cage effect" on the mechanism of reversible bimolecular multistage chemical reactions in solutions

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Manifestations of the "cage effect" at the encounters of reactants are theoretically treated by the example of multistage reactions in liquid solutions including bimolecular exchange reactions as elementary stages. It is shown that consistent consideration of quasi-stationary kinetics of multistage reactions (possible only in the framework of the encounter theory) for reactions proceeding near reactants contact can be made on the basis of the concepts of a "cage complex." Though mathematically such a consideration is more complicated, it is more clear from the standpoint of chemical notions. It is established that the presence of the "cage effect" leads to some important effects not inherent in reactions in gases or those in solutions proceeding in the kinetic regime, such as the appearance of new transition channels of reactant transformation that cannot be caused by elementary event of chemical conversion for the given mechanism of reaction. This results in that, for example, rate constant values of multistage reaction defined by standard kinetic equations of formal chemical kinetics from experimentally measured kinetics can differ essentially from real values of these constants. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4928640]

I. INTRODUCTION

It is generally accepted that the mechanism of multistage reaction (a combination of consecutive and parallel elementary reactions) unambiguously determines the set of kinetic equations of formal chemical kinetics[1] based on the kinetic law of mass action. According to this law, concentration variation rate of any of reactants is specified by the sum of concentration variation rates in the process of all elementary reactions leading to disappearance or production of this reactant. For bimolecular reactions occurring in rather rarefied gas or dilute solution (when the reaction proceeds with the participation of just two molecules), the rate of such a variation (negative for the case of reactant disappearance or positive in the case of its formation) is proportional to the product of concentrations of reacting particles. However, though the course of rather fast reactions (for example, reactions between radicals) in liquid solutions depends on mobility of reactants causing them to approach closely enough for chemical conversion elementary event to take place, and solution resembles "gas" of reactants dissolved in chemically inert solvent, there is crucial difference between reactions in gases and liquids.

In gases usually considered in the context of collision theory, any reaction rate constant value is determined by corresponding inelastic scattering cross section on collision.[2-4]

In dilute solutions (as in gases), reactants are mainly in the process of free random walks (i.e., at distances insufficient for chemical transformation elementary event to occur). However, the difference is that the character of reactant motion changes due to the presence of the solvent (commonly such a motion is treated as continual diffusion). It is essential that the change in the character of reactant motion affects the character of chemical transformation course on the approach of reactants. This is mostly easily seen if we consider the so-called contact reactions, i.e., reactions occurring between reactants that approached to the distances equal to the sum of van der Waals radii. The reason is that reactants coming in contact which leads to chemical conversion event do not go to the bulk after the end of the contact, but (due to the "cage effect"[5,6]) can re-contact thus giving rise to further chemical transformation. Only after a series of re-contacts reactants move apart, and this corresponds to the escape from the "cage," i.e., the products begin walking freely in the bulk. So the process that in gas is considered as collision, in solution is treated as the encounter (residence in the "cage") of reactants (analog of "scattering") consisting of a number of re-contacts. Just for this reason, the theory based on understanding of solution as "gas" of reactants received the name the encounter theory.[7-9] For a long time (up to the development of consistent many-particle derivations of kinetic equations started in the late 1980s of the last century), such a theory has been the only one able to calculate the kinetics of diffusion-influenced elementary reversible bimolecular and multistage physicochemical processes. As is known,[10] when examining the kinetics of the simplest elementary irreversible bimolecular reactions, the encounter theory gives the Waite-Smoluchowski equations. In this case, calculation of quasi-stationary kinetics may be performed using the concepts of quasi-stationary "cage complex" in the framework of formal chemical kinetics.[11] However, application of such concepts to the consideration of multistage reactions is not obvious and has been substantiated just recently on the basis of the encounter theory solely for the case of two-stage contact reactions between spherical

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reactants.[12] Generalization of these concepts to a wide class of bimolecular exchange reaction abandoning rough physical assumptions in the models of the structure of reactants, their reactivity, and molecular motion (including rotation) is one of the goals of the present work.

The presence of the "cage effect" gives rise to a number of specific features of reactions in liquid solutions, the examination of which is the subject of this contribution as well. In particular, in the course of consecutive multistage reaction, the influence of reactant mobility does not reduce only to traditional redefinition of rate constants of elementary stages[9,13–15] but can change radically the set of equations of formal chemical kinetics, i.e., it results in additional terms in kinetic equations entirely determined by reactant motion. Since the analysis of such kinetic equations is used to define rate constants by fitting of experimental kinetics, the above change may turn to be crucial. First, this fact was demonstrated in paper[15] in studies of irreversible consecutive multistage bimolecular exchange reactions, and then it was discovered in theoretical treatment of multisite binding and catalysis processes in biological reactions.[16]

In Sec. II of the article, we establish the correspondence between the encounter theory notions and the "cage complex" method for elementary reversible reaction $A_1 + B_1 \leftrightarrow A_2 + B_2$. Equations of formal chemical kinetics of this reaction are derived, rate constants are determined with allowance for the "cage effect," and physical interpretation of the results is made. Section III deals with reversible two-stage reaction $A_1 + B_1 \leftrightarrow A_2 + B_2 \leftrightarrow A_3 + B_3$ demonstrating the change in the reaction mechanism in going from kinetic control to diffusion one. Physical (based on the encounter theory) and chemical (based on the "cage complex" method) interpretation of the results is given. Section IV presents generalization of the results to bimolecular multistage reaction containing an arbitrary number of reversible bimolecular exchange reactions between nonidentical reactants as elementary stages. The results are summarized in Section V.

II. ELEMENTARY REVERSIBLE BIMOLECULAR REACTIONS (STAGES OF MULTISTAGE REACTIONS)

A. The encounter theory

First, consider the stages (elementary bimolecular reactions) of multistage reaction. For elementary bimolecular reversible reaction

$$A_1 + B_1 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A_2 + B_2, \tag{2.1}$$
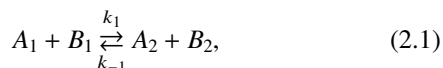
the set of equations of formal chemical kinetics is[1]

$$\frac{d}{dt}[A_1]_t = \frac{d}{dt}[B_1]_t = -k_1[A_1]_t[B_1]_t + k_{-1}[A_2]_t[B_2]_t,$$

$$\frac{d}{dt}[A_2]_t = \frac{d}{dt}[B_2]_t = k_1[A_1]_t[B_1]_t - k_{-1}[A_2]_t[B_2]_t. \tag{2.2}$$

Further, following the scattering theory terminology, we introduce the concept of reaction channel implying a group of reactants. In our case, we have two channels $A_1 + B_1$ and $A_2 + B_2$. Besides, it is convenient, following Ref. 17, to

introduce the concept of transition channels. In the kinetic scheme considered on the basis of kinetic equations (2.2) of formal chemical kinetics, there are two of them: forward transition channel (transition from the first channel to the second one) and back transition channel (transition from the second channel to the first one). Then, k_1 is the rate constant of forward transition, and k_{-1} of the back one.

As a rule, the equations of formal chemical kinetics assume that in liquid solution the reaction in question proceeds in the so-called kinetic regime, when the reaction course is entirely controlled by the elementary event rate on approach of reactants to the distance at which the reaction is possible. In this case, rate constants k_1 and $k_2 = k_{-1}$ are equal to reaction constants specified by elementary event rates. In the general case, elementary event probabilities (defining forward and back chemical transformation rates) depend on two coordinates: relative coordinates of the initial pair and relative coordinates of the produced pair. By the coordinates of reactant pairs, we mean the coordinate q of the configuration space which includes both relative-position vector and orientation angles of reactants. For forward transition channel, this probability is defined by the function $w_1(q|q')$ specifying the probability density (per unit of time) of the formation of reaction products A_2 and B_2 with the coordinate q from initial reactants A_1 and B_1 with the coordinate q'. For back transition channel, this probability is defined by the function $w_{-1}(q'|q)$ determining the probability density (per unit of time) of the formation of reactants A_1 and B_1 with the coordinate q' from a pair of reactants A_2 and B_2 with the coordinate q of the second channel. The most commonly used elementary event rates $w_1(q)$ and $w_{-1}(q)$ defining complete reaction rate in the given transition channel are obtained from the quantities introduced by integration over the produced pair coordinate

$$w_1(q) = \int w_1(q'|q)\,dq',$$

$$w_{-1}(q) = \int w_{-1}(q'|q)\,dq'. \tag{2.3}$$

Reaction constants are found as

$$k_1 = \iint w_1(q'|q)\,\varphi_1(q)dq'dq \equiv \int w_1(q)\varphi_1(q)dq,$$

$$k_{-1} = \iint w_{-1}(q'|q)\,\varphi_2(q)dq'dq \equiv \int w_{-1}(q)\varphi_2(q)dq, \tag{2.4}$$

where $\varphi_1(q)$ and $\varphi_2(q)$ are equilibrium coordinate q distributions (determined by the force interactions between reactants in the corresponding channels). The introduced elementary event probability densities $w_1(q|q')$ and $w_{-1}(q'|q)$ allow for possible change of the pair coordinates due to reaction (rebound effect) and satisfy the kinetic principle of detailed balance[17]

$$\frac{w_1(q|q')\,\varphi_1(q')}{k_1} = \frac{w_{-1}(q'|q)\,\varphi_2(q)}{k_{-1}}. \tag{2.5}$$

For simplicity, in further discussion, we neglect the rebound effect, as in most of the approaches available in the literature (since it makes no essential influence on the results), i.e., we

put

$$w_1(q'|q) = w_1(q)\delta(q'-q),$$
$$w_{-1}(q'|q) = w_{-1}(q)\delta(q'-q). \qquad (2.6)$$

Here, and further, $\delta(q'-q)$ is Dirac delta-function. In this case, the kinetic principle of detailed balance (2.5) can be written as

$$\psi_1(q)\varphi_1(q) \equiv \frac{w_1(q)\varphi_1(q)}{k_1} = \psi_2(q)\varphi_2(q) \equiv \frac{w_{-1}(q)\varphi_2(q)}{k_{-1}}. \qquad (2.7)$$

Here, we introduce normalized functions $\psi_1(q)$ and $\psi_2(q)$

$$\int \psi_1(q)\varphi_1(q)\,dq = 1, \qquad \int \psi_2(q)\varphi_2(q)\,dq = 1 \qquad (2.8)$$

to be used further. Each of them we shall call the shape of the corresponding reaction zone. Elementary transformation rates (2.3) can be represented as

$$w_1(q) = k_1\psi_1(q), \quad w_{-1}(q) = k_{-1}\psi_2(q). \qquad (2.9)$$

However, if the rate of such transformations is significant, then the reaction course will be affected by the process of the approach of reactants in solution, i.e., their motion (commonly treated as continual diffusion). In this case, the description is based on the theory of diffusion influenced reactions. Originally, such a theory was developed just for irreversible one-stage reactions,[13,14] and before the appearance of modern many-particle derivations of kinetic equations (see review articles[9,17] and references herein), the encounter theory was the only theory able to describe reversible (including multistage) reactions.[8,9] According to this theory, residence of reactants of species A_1 or A_2 in the reacting system is considered as being in states 1 or 2 of "effective" particle $\mathcal{A}$, and reactants of species B_1 or B_2 in the corresponding states of "effective" particle B. So let us introduce the column vectors of concentrations $[A_i]_t$ $(i = 1, 2)$, $[B_k]_t$ $(k = 1, 2)$ in the basis of individual states of "effective" particles

$$[\mathbf{A}]_t = \begin{pmatrix} [A_1]_t \\ [A_2]_t \end{pmatrix}, \qquad [\mathbf{B}]_t = \begin{pmatrix} [B_1]_t \\ [B_2]_t \end{pmatrix}. \qquad (2.10)$$

Collective basis (ik) of two particles has four states that can be marked by Roman numerals. However, since the reaction at hand leads to transitions only between collective states $(11) = I$ and $(22) = II$, one can consider just a restricted basis and use Arabic numerals for states and channels. Then, the elementary event rates and motion operators' matrices (Liouvillians) in this collective states basis are

$$\hat{\mathbf{W}} = \begin{pmatrix} -w_1(q) & w_{-1}(q) \\ w_1(q) & -w_{-1}(q) \end{pmatrix}, \quad \hat{\mathbf{L}}_q = \begin{pmatrix} \hat{\mathcal{L}}_q^{(1)} & 0 \\ 0 & \hat{\mathcal{L}}_q^{(2)} \end{pmatrix}, \qquad (2.11)$$

where $w_1(q)$ and $w_{-1}(q)$ are elementary event rates (2.9) of the first and the second (back reaction) elementary stages of reaction (2.1), respectively, and $\hat{\mathcal{L}}_q^{(i)}$ is the relative motion operator of reactants A_i and B_i $(i = 1, 2)$.

Now we use general quasi-stationary vector equation of the encounter theory[9]

$$\frac{d}{dt}[\mathbf{A}]_t = Tr_B \int \hat{\mathbf{W}}(q)\,\hat{\mathbf{G}}(q)dq\,([\mathbf{A}]_t \otimes [\mathbf{B}]_t), \quad (2.12)$$

where $\otimes$ means the direct product of concentration vectors and Tr_B is the trace (summation) over states B_i. Similar equation also takes place for "effective particles" B. This equation describes variation of reactants concentrations at the times of free random walks (as the transient stage ends), where concentrations commonly change finally attaining their equilibrium values. The steady-state Liouvillian of the pair densities is the stationary solution $\hat{\mathbf{G}}(q) = \lim_{t\to\infty} \hat{\mathbf{G}}(q,t)$ of the matrix equation defining the change in these densities due to the encounter of reactants

$$\frac{\partial}{\partial t}\hat{\mathbf{G}}(q,t) = \hat{\mathbf{W}}(q)\hat{\mathbf{G}}(q,t) + \hat{\mathbf{L}}_q\,\hat{\mathbf{G}}(q,t), \qquad (2.13)$$

with the initial conditions $\hat{\mathbf{G}}(q,0) = \hat{\boldsymbol{\varphi}}_{eq}(q)$, where $\hat{\boldsymbol{\varphi}}_{eq}(q)$ is diagonal matrix with elements equal to equilibrium coordinate q distributions $\varphi_1(q)$ and $\varphi_2(q)$.

Note that the replacement of the steady-state Liouvillian of the pair density $\hat{\mathbf{G}}(q)$ in Eq. (2.12) by its time dependent value $\hat{\mathbf{G}}(q,t)$ from Eq. (2.13) makes it possible to allow for time dependence of kinetic coefficients, i.e., to take into account variation of concentrations at the encounter times (transient stage). It is essential that in binary approximation such binary non-Markovian (with time dependent rate constants) differential rate equations for bimolecular reactions are completely equivalent to integro-differential equations (of convolution type) obtained by many-particle methods.[9] However, it is required that the characteristic encounter times of reactants (in any channel) be considerably less than the mean encounter times of reactants in any channel of multistage reaction. Violation of this condition necessary for the applicability of the encounter theory (the collision theory analog) in the consideration of bimolecular reactions in dilute solutions is possible only in the case where mobilities in different channels sharply differ (when the characteristic encounter time in some channel becomes comparable with or less than the mean time between the encounters of reactants in some channel) which is an extraordinary situation.

Violation of the encounter theory applicability condition is also possible if we include in the consideration the processes of monomolecular transformations (for example, spontaneous decay in fluorescence quenching), or dissociative stages. In this case, by the mean times of free random walks, one should understand the mean lifetime of reactants (that undergo monomolecular transformation or dissociation).[17] The rate of such processes does not depend on concentration of reactants, so smallness of the density parameter is insufficient for the encounter theory applicability conditions to be fulfilled. Just in these cases, it is necessary to use integro-differential (convolution type) equations.[9,17,18] Examination of such reactions is not the subject of the present work.

Thus, in the framework of the encounter theory which is binary by definition (i.e., is confined to the consideration of pair encounters applicable in dilute solutions), the characteristic encounter times are essentially less than the mean times

between the encounters, so the transient stage can be neglected. Then, vector kinetic equation (2.12) corresponds to a set of differential equations with constant coefficients (steady-state rate constants). These (the so-called Markovian) kinetic equations describe chemical kinetics of the class of reactions under study over almost the entire range of binary kinetics.[9,17] Exactly, these equations are widely used in kinetics simulation of multistage biological reactions.

Let us introduce simplified designations for matrix elements of the Liouvillian $\hat{\mathbf{G}}(q)$,

$$
\begin{aligned}
G_{\mathrm{I\,I}}(q) &\equiv G_{11}(q) = n_1(q) = n_1^+(q)\varphi_1(q),\\
G_{\mathrm{I\,II}}(q) &\equiv G_{12}(q) = m_2(q) = m_2^+(q)\varphi_1(q),\\
G_{\mathrm{II\,I}}(q) &\equiv G_{21}(q) = m_1(q) = m_1^+(q)\varphi_2(q),\\
G_{\mathrm{II\,II}}(q) &\equiv G_{22}(q) = n_2(q) = n_2^+(q)\varphi_2(q).
\end{aligned}
\tag{2.14}
$$

Along with matrix elements of the Liouvillian $\hat{\mathbf{G}}(q)$, in Eqs. (2.14), we introduce adjoint elements[15] marked by the upper cross. Note that quantities $n_1(q)$ and $m_2(q)$ are responsible for concentration variation in the first channel ($A_1 + B_1$), and quantities $n_2(q)$ and $m_1(q)$ in the second channel ($A_2 + B_2$).

From Eqs. (2.12) and (2.14), we obtain kinetic equations similar to Eqs. (2.2) of formal chemical kinetics

$$
\begin{aligned}
\frac{d[A_1]_t}{dt} &= \frac{d[B_1]_t}{dt} = -k_{11}[A_1]_t[B_1]_t + k_{12}[A_2]_t[B_2]_t,\\
\frac{d[A_2]_t}{dt} &= \frac{d[B_2]_t}{dt} = k_{21}[A_1]_t[B_1]_t - k_{22}[A_2]_t[B_2]_t.
\end{aligned}
\tag{2.15}
$$

However, the rate constants appearing in it are not determined solely by elementary event rates but are as follows:

$$
\begin{aligned}
k_{11} &= k_{21} = \int \left(w_1(q)n_1(q) - w_{-1}(q)m_1(q) \right) dq,\\
k_{22} &= k_{12} = \int \left(w_{-1}(q)n_2(q) - w_1(q)m_2(q) \right) dq,
\end{aligned}
\tag{2.16}
$$

i.e., they are expressed in terms of stationary solutions $n_1(q)$, $m_1(q)$, $n_2(q)$, $m_2(q)$ of the equations following from Eqs. (2.13) and (2.14):

$$
\begin{aligned}
\frac{\partial}{\partial t} n_1(q,t) &= -w_1(q)\,n_1(q,t) + w_{-1}(q)m_1(q,t)\\
&\quad + \hat{\mathcal{L}}_q^{(1)} n_1(q,t),\\
\frac{\partial}{\partial t} m_1(q,t) &= w_1(q)\,n_1(q,t) - w_{-1}(q)m_1(q,t)\\
&\quad + \hat{\mathcal{L}}_q^{(2)} m_1(q,t),
\end{aligned}
\tag{2.17a}
$$

and

$$
\begin{aligned}
\frac{\partial}{\partial t} n_2(q,t) &= -w_{-1}(q)\,n_2(q,t) + w_1(q)m_2(q,t)\\
&\quad + \hat{\mathcal{L}}_q^{(2)} n_2(q,t),\\
\frac{\partial}{\partial t} m_2(q,t) &= w_{-1}(q)\,n_2(q,t) - w_1(q)m_2(q,t)\\
&\quad + \hat{\mathcal{L}}_q^{(1)} m_2(q,t),
\end{aligned}
\tag{2.17b}
$$

with the initial conditions

$$
\begin{aligned}
n_1(q,0) &= \varphi_1(q),\quad n_2(q,0) = \varphi_2(q),\\
m_1(q,0) &= m_2(q,0) = 0.
\end{aligned}
$$

Note that reaction interactions relate pairs of quantities $n_i(q)$, $m_i(q)$ ($i = 1,2$), belonging to different channels (forward and back) of the reaction. For further consideration, it will be convenient to represent stationary equations obtained from Eqs. (2.17) in the integral form using free Green functions $g_{01}(q\,|q')$ and $g_{02}(q\,|q')$ that obey the well-known equations

$$
-\hat{\mathcal{L}}_q^{(i)}\, g_{0i}(q\,|q') = \delta(q - q')\quad (i = 1,2)
\tag{2.18}
$$

and satisfy the detailed balance relation

$$
g_{0i}(q'\,|q)\,\varphi_i(q) = g_{0i}(q\,|q')\,\varphi_i(q')\quad (i = 1,2).
\tag{2.19}
$$

Each of these functions is readily seen to describe the free motions of the corresponding pairs (without reactions), translational and rotational, and are the time integrals

$$
g_{0i}(q\,|q') = \int_0^\infty \varphi_i(q,t\,|q',0)\,dt\quad (i = 1,2)
\tag{2.20}
$$

of the conditional probability densities $\varphi_i(q,t\,|q',0)$ ($i = 1,2$) to have configuration coordinate q at the time moment t if it was q' at the initial time moment $t = 0$. Then, the desired stationary equations for adjoint quantities obtained from Eqs. (2.17) in view of Eqs. (2.9) and (2.19) have the form

$$
\begin{aligned}
n_1^+(q) &= 1 - k_1 \int g_{01}(q'|q)\psi_1(q')n_1^+(q')dq'\\
&\quad + k_{-1} \int g_{01}(q'|q)\psi_2(q')\frac{\varphi_2(q')}{\varphi_1(q')}m_1^+(q')dq',\\
m_1^+(q) &= k_1 \int g_{02}(q'|q)\psi_1(q')\frac{\varphi_1(q')}{\varphi_2(q')}n_1^+(q')dq'\\
&\quad - k_{-1} \int g_{02}(q'|q)\psi_2(q')m_1^+(q')dq',
\end{aligned}
\tag{2.21a}
$$

and

$$
\begin{aligned}
n_2^+(q) &= 1 - k_{-1} \int g_{02}(q'|q)\psi_2(q')n_2^+(q')dq'\\
&\quad + k_1 \int g_{02}(q'|q)\psi_1(q')\frac{\varphi_1(q')}{\varphi_2(q')}m_2^+(q')dq',\\
m_2^+(q) &= k_{-1} \int g_{01}(q'|q)\psi_2(q')\frac{\varphi_2(q')}{\varphi_1(q')}n_2^+(q')dq'\\
&\quad - k_1 \int g_{01}(q'|q)\psi_1(q')m_2^+(q')dq'.
\end{aligned}
\tag{2.21b}
$$

Then, let us introduce the averaging of some quantity $A(q)$ over the reaction zones,

$$
\begin{aligned}
\langle A(q)\rangle &\equiv (A(q)\,|\psi_1(q)) = \int A(q)\,\psi_1(q)\varphi_1(q)dq\\
&= (A(q)\,|\psi_2(q)) = \int A(q)\,\psi_2(q)\varphi_2(q)\,dq.
\end{aligned}
\tag{2.22}
$$

It can be considered as a scalar product of the functions $A(q)$ and $\psi_1(q)$ with the weight $\varphi_1(q)$ or $\psi_2(q)$ with the weight $\varphi_2(q)$. Note that owing to detailed balance condition (2.7), the results of averaging over any of two reaction zones coincide.

Now we can define the quantities

$$\upsilon_i = \langle \psi_i(q) \rangle^{-1} \equiv (\psi_i(q) | \psi_i(q))^{-1},$$
$$\tau_{ci}(q) = \upsilon_i \int \psi_i(q') g_{0i}(q'|q) d\,q' \quad (i = 1, 2), \tag{2.23}$$

which are the corresponding reaction zone volumes and the mean residence times in the reaction zones for the starting position q.[19–21] It is of interest that reaction constants can be represented as products of the mean rates of elementary event and reaction volumes

$$k_1 = \langle w_1(q) \rangle \upsilon_1, \qquad k_{-1} = \langle w_{-1}(q) \rangle \upsilon_2, \tag{2.24}$$

and rate constants (2.16) as

$$k_{11} = k_{21} = k_1 \langle n_1^+(q) \rangle - k_{-1} \langle m_1^+(q) \rangle,$$
$$k_{22} = k_{12} = k_{-1} \langle n_2^+(q) \rangle - k_1 \langle m_2^+(q) \rangle. \tag{2.25}$$

Averaging of both parts of Eqs. (2.21) over the corresponding reaction zones with the use of Eqs. (2.23) gives

$$\langle n_1^+(q) \rangle = 1 - \frac{k_1}{\upsilon_1} \langle \tau_{c1}(q) n_1^+(q) \rangle + \frac{k_{-1}}{\upsilon_1} \langle \tau_{c1}(q) m_1^+(q) \rangle,$$
$$\langle m_1^+(q) \rangle = \frac{k_1}{\upsilon_2} \langle \tau_{c2}(q) n_1^+(q) \rangle - \frac{k_{-1}}{\upsilon_2} \langle \tau_{c2}(q) m_1^+(q) \rangle, \tag{2.26a}$$

and

$$\langle n_2^+(q) \rangle = 1 - \frac{k_{-1}}{\upsilon_2} \langle \tau_{c2}(q) n_2^+(q) \rangle + \frac{k_1}{\upsilon_2} \langle \tau_{c2}(q) m_2^+(q) \rangle,$$
$$\langle m_2^+(q) \rangle = \frac{k_{-1}}{\upsilon_1} \langle \tau_{c1}(q) n_2^+(q) \rangle - \frac{k_1}{\upsilon_1} \langle \tau_{c1}(q) m_2^+(q) \rangle. \tag{2.26b}$$

Now we use the decoupling procedure[9,19,21]

$$\langle \tau_{ci}(q) n_k^+(q) \rangle \approx \langle \tau_{ci}(q) \rangle \langle n_k^+(q) \rangle \equiv \tau_{ci} \langle n_k^+(q) \rangle,$$
$$\langle \tau_{ci}(q) m_k^+(q) \rangle \approx \langle \tau_{ci}(q) \rangle \langle m_k^+(q) \rangle \equiv \tau_{ci} \langle m_k^+(q) \rangle; \tag{2.27}$$
$$(i, k = 1, 2),$$

where

$$\tau_{ci} = \langle \tau_{ci}(q) \rangle = \upsilon_i \iint \psi_i(q') g_{0i}(q'|q) \psi_i(q)$$
$$\times \varphi_i(q) d\,q' d\,q \quad (i = 1, 2) \tag{2.28}$$

are the complete mean residence times in the corresponding reaction zone (the mean residence time in the reaction zone for the starting position q averaged over the starting positions in the reaction zone). Note that procedure (2.27) is exact in the case of spherically symmetric contact reactivity.[21] When the reaction takes place in a narrow reaction zone, Eqs. (2.27) are the approximation that can be shown to require that the dispersion of any mean residence times $\tau_{ci}(q)$ be small compared to the square of complete mean residence time

$$d_i = \langle \tau_{ci}^2(q) \rangle - \langle \tau_{ci}(q) \rangle^2$$
$$= \langle (\tau_{ci}(q) - \langle \tau_{ci}(q) \rangle)^2 \rangle \ll \langle \tau_{ci}(q) \rangle^2 = \tau_{ci}^2. \tag{2.29}$$

Decoupling (2.27) is the basis of the so-called kinematic approximation used in the theory of mobility influenced reactions[21] similar to the so-called closure approximation.[19,22] In this approximation, we can introduce, along with representation (2.24) for the reaction constants k_1 and k_{-1}, similar

representation for the reaction rate constants in mobility controlled regime (diffusion constants in the case of continual diffusion),[19,21]

$$k_{di} = \frac{\upsilon_i}{\tau_{ci}} \quad (i = 1, 2). \tag{2.30}$$

Then, Eqs. (2.26a), in view of Eqs. (2.27) and (2.30), and the first Eq. (2.25) can be written as

$$\langle n_1^+(q) \rangle = 1 - \frac{k_1}{k_{d1}} \langle n_1^+(q) \rangle + \frac{k_{-1}}{k_{d1}} \langle m_1^+(q) \rangle \equiv 1 - \frac{k_{11}}{k_{d1}},$$
$$\langle m_1^+(q) \rangle = \frac{k_1}{k_{d2}} \langle n_1^+(q) \rangle - \frac{k_{-1}}{k_{d2}} \langle m_1^+(q) \rangle \equiv \frac{k_{11}}{k_{d2}} = \frac{k_{21}}{k_{d2}}, \tag{2.31a}$$

and give, with allowance for the first Eq. (2.25), the closed equation for the definition $k_{11} = k_{21}$

$$k_{11} = k_1 - \frac{k_1}{k_{d1}} k_{11} - \frac{k_{-1}}{k_{d2}} k_{11} \quad \text{or}$$
$$k_{11} = \frac{k_1}{1 + \frac{k_1}{k_{d1}} + \frac{k_{-1}}{k_{d2}}} = k_{21}. \tag{2.31b}$$

Eqs. (2.26b) (taking account of Eqs. (2.27) and (2.30), and the second Eq. (2.25)) can be written as

$$\langle n_2^+(q) \rangle = 1 - \frac{k_{-1}}{k_{d2}} \langle n_2^+(q) \rangle + \frac{k_1}{k_{d2}} \langle m_2^+(q) \rangle \equiv 1 - \frac{k_{22}}{k_{d2}},$$
$$\langle m_2^+(q) \rangle = \frac{k_{-1}}{k_{d1}} \langle n_2^+(q) \rangle + \frac{k_1}{k_{d1}} \langle m_2^+(q) \rangle \equiv \frac{k_{22}}{k_{d1}} = \frac{k_{12}}{k_{d1}}, \tag{2.32a}$$

and give, in view of the second Eq. (2.25), the closed equation for the definition $k_{22} = k_{12}$

$$k_{22} = k_{-1} - \frac{k_{-1}}{k_{d2}} k_{22} - \frac{k_1}{k_{d1}} k_{22} \quad \text{or}$$
$$k_{22} = \frac{k_{-1}}{1 + \frac{k_1}{k_{d1}} + \frac{k_{-1}}{k_{d2}}} = k_{12}. \tag{2.32b}$$

This expression at $k_{d1} = k_{d2}$ is formally similar to the well-known expression for spherically symmetric contact reactions.[7] However, expressions (2.31b) and (2.32b) are an essential generalization to the case of arbitrary non-isotropic reactivity and mobility of reactants (including rotation).

Note that kinetic equations (2.15) for diffusion-influenced reaction (2.1) have the same form of kinetic equations of formal chemical kinetics as Eqs. (2.2) for the same reaction in the kinetic regime. The only difference is in redefinition of the corresponding rate constants in accordance with Eqs. (2.31b) and (2.32b). Thus, from the standpoint of chemical kinetics, taking account of the influence of reactants motion in solution (normally, diffusion) has no effect on the mechanism of the reaction under study; it just redefines the rates of elementary stages (direct and back transition channels).

B. The "cage complex" method

Thus, the encounter theories allow one to easily derive kinetic equations (2.15) coinciding with kinetic equations of

formal chemical kinetics (2.2) (for reactions proceeding in the kinetic regime) and calculate the required steady-state rate constants with allowance for diffusion influence. However, it seems interesting to see whether the exact kinetic equations thus obtained may be derived on the basis of simple kinetic scheme relying on the concepts of the "cage complex." First, such concepts have been applied in the examination of the simplest irreversible reaction.[11]

Introduce the concentrations of the states of "cage complex" in the following way:

$$
\begin{aligned}
[A_1 \ldots B_1] &= \upsilon_1 \big(\langle n_1^+(q) \rangle \, [A_1]_t [B_1]_t \\
&\quad + \langle m_2^+(q) \rangle \, [A_2]_t [B_2]_t \big), \\
[A_2 \ldots B_2] &= \upsilon_2 \big(\langle n_2^+(q) \rangle \, [A_2]_t [B_2]_t \\
&\quad + \langle m_1^+(q) \rangle \, [A_1]_t [B_1]_t \big).
\end{aligned}
\tag{2.33}
$$

Note that each state of "cage complex" includes pair densities from different pairs of closed equations (2.31a) and (2.32a). Just as it must be, the state $A_1 \ldots B_1$ of the "cage complex"
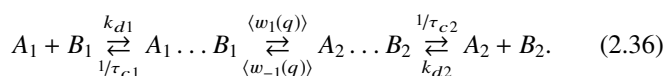
involves the averaged pair densities $n_1^+(q)$ and $m_2^+(q)$, the motion of which, as is seen from Eq. (2.17), is described by the operator $\hat{\mathcal{L}}_q^{(1)}$ of the initial pair of reactants. Accordingly, the state $A_2 \ldots B_2$ of the "cage complex" contains the averaged pair densities $n_2^+(q)$ and $m_1^+(q)$, the motion of which, as is seen from Eq. (2.17), is described by the operator $\hat{\mathcal{L}}_q^{(2)}$ of a pair of reactants formed by forward reaction of a pair of reactants. With Eq. (2.30), the last equalities in Eqs. (2.31a) and (2.32a), and definitions (2.33), kinetic Eq. (2.15) with allowance for definitions (2.25) of their kinetic coefficients may be recast as

$$
\frac{d}{dt}[A_1]_t = \frac{d}{dt}[B_1]_t = -k_{d1}[A_1]_t[B_1]_t + \tfrac{1}{\tau_{c1}}[A_1 \ldots B_1]_t,
$$

$$
\frac{d}{dt}[A_2]_t = \frac{d}{dt}[B_2]_t = -k_{d2}[A_2]_t[B_2]_t + \tfrac{1}{\tau_{c2}}[A_2 \ldots B_2]_t.
\tag{2.34}
$$

Using definitions (2.33) of the concentrations of the states of the "cage complex" and Eqs. (2.31a) and (2.32a), we easily see that the following equations take place:

$$
\frac{d}{dt}[A_1 \ldots B_1]_t \approx 0 = k_{d1}[A_1]_t[B_1]_t - \big(\langle w_1(q) \rangle + \tfrac{1}{\tau_{c1}} \big)[A_1 \ldots B_1]_t + \langle w_{-1}(q) \rangle [A_2 \ldots B_2]_t,
$$

$$
\frac{d}{dt}[A_2 \ldots B_2]_t \approx 0 = k_{d2}[A_2]_t[B_2]_t + \langle w_1(q) \rangle [A_1 \ldots B_1]_t - \big(\langle w_{-1}(q) \rangle + \tfrac{1}{\tau_{c2}} \big)[A_2 \ldots B_2]_t,
\tag{2.35}
$$

i.e., concentrations of the states of the "cage complex" are found as quasi-stationary solutions of kinetic equations (2.35). Equations (2.34) define concentration variation of reactants in the corresponding channels both due to the formation of the "cage complex" as a result of the encounters, and due to the disruption of this complex resulting from spatial separation of reactants of pairs $A_1 \ldots B_1$ or $A_2 \ldots B_2$ caused by their motion. Equation (2.35) describe concentration variation of the states $A_1 \ldots B_1$ and $A_2 \ldots B_2$ of the "cage complex" determined by production of pairs on encounters, their spatial separation due to motion, as well as their mutual transformation as a result of reversible reaction. The equations are in complete agreement with equations of formal chemical kinetics for a simple kinetic scheme

$$
A_1 + B_1 \underset{1/\tau_{c1}}{\overset{k_{d1}}{\rightleftarrows}} A_1 \ldots B_1 \underset{\langle w_{-1}(q) \rangle}{\overset{\langle w_1(q) \rangle}{\rightleftarrows}} A_2 \ldots B_2 \underset{k_{d2}}{\overset{1/\tau_{c2}}{\rightleftarrows}} A_2 + B_2.
\tag{2.36}
$$

It differs from the corresponding scheme[15] of irreversible reaction in that the initial reactants A_1 and B_1, as well as the products A_2 and B_2 which are in the process of free walks in solution due to diffusion (in the general case, relative diffusion coefficients for initial reactants and products differ) encounter to form a "cage" (with rate constants k_{d1} and k_{d2}, respectively), the escape from which proceeds at the rates $1/\tau_{c1}$ or $1/\tau_{c2}$ depending on the state in which the "cage complex" is $A_1 \ldots B_1$ or $A_2 \ldots B_2$. The "cage" complex is not the whole encounter of reactants (consisting of re-contacts) but just a part of it, when reactants are in contacts,

$$
A_1 \ldots B_1 \underset{\langle w_{-1}(q) \rangle}{\overset{\langle w_1(q) \rangle}{\rightleftarrows}} A_2 \ldots B_2,
\tag{2.37}
$$
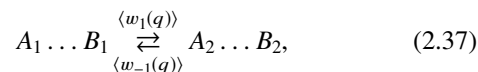
at which reversible chemical transformation of reactants takes place at the rates $\langle w_1(q) \rangle$ of forward and $\langle w_{-1}(q) \rangle$ back processes, respectively. So from the standpoint of the encounter theory, it makes no difference which reactants A_1 or A_2 encounter in solution with reactants B_1 or B_2, and "contact" complexes $A_1 \ldots B_1$ and $A_2 \ldots B_2$ are different states of one "cage complex."

Similar reaction schemes are often used in chemical kinetics for empirical calculations of reaction rate constants in gases (e.g., for reactions proceeding via long-lived complex). However, a remarkable advantage of the reaction scheme with appropriately defined kinetic coefficients k_{d1}, k_{d1}, τ_{c1}, τ_{c2}, $\langle w_1(q) \rangle$, and $\langle w_1(q) \rangle$ (that are determined by the reaction sink terms $w_1(q)$ and $w_{-1}(q)$, the operator $\hat{\mathcal{L}}_q^{(1)}$ or $\hat{\mathcal{L}}_q^{(2)}$ (or free Green functions $g_{01}(q|q')$ and $g_{02}(q|q')$ of reactant mobility)) is the possibility to solve (with the controlled accuracy) a complicated problem of mobility influenced reactions in solutions. The initial exact equations of the encounter theory (Eqs. (2.15), (2.25), (2.31a), and (2.32a)) are even easier to solve than kinetic equations (2.34) and (2.35) of kinetic scheme (2.36). However, Eqs. (2.34) and (2.35) are very useful from the point of view of clear chemical interpretation of the results derived.

Note that the applicability of the above simple kinetic scheme means that the distributions $f_i(\tau)$ $(i = 1, 2)$ in complete residence times (in each state) in the reaction

zones ("contact complexes" lifetimes) are Poisson ($f_i(\tau)$ = $^1/_{\tau_{ci}} \exp(-\tau/\tau_{ci})$). Such notions correspond to the familiar exponential model. Though the distribution in the encounter times (residence in the "cage") is not exponential,[9] its applicability is related to the fact that in the absence of physicochemical processes between re-contacts, the efficiency of a quasi-steady reaction is determined by complete residence times of all contacts on the encounter of the given reactants A_i and B_i, and such a time distribution is exponential. We shall call the above method of the derivation of the Markovian kinetic equations based on a simple formal kinetic scheme of the reaction course, the "cage complex" method. Thus, in the framework of both methods, we have

$$k_{11} = k_{21} = \frac{k_1 k_{d1} k_{d2}}{k_{d1_1} k_{d2} + k_1 k_{d2} + k_{-1} k_{d1}} \equiv k_{d1} p_1,$$

$$k_{22} = k_{12} = \frac{k_{-1} k_{d1} k_{d2}}{k_{d1_1} k_{d2_2} + k_1 k_{d2} + k_{-1} k_{d1}} \equiv k_{d2} p_{-1}, \quad (2.38)$$
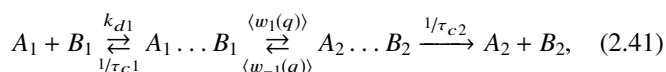
where the encounter efficiencies are introduced

$$p_1 = \frac{k_1/k_{d1}}{1 + k_1/k_{d1} + k_{-1}/k_{d2}},$$

$$p_{-1} = \frac{k_{-1}/k_{d2}}{1 + k_1/k_{d1} + k_{-1}/k_{d2}}. \quad (2.39)$$

It is seen that each of rate constants $k_{11} = k_{21}$ and $k_{22} = k_{12}$ depends on direct and inverse reaction constants k_1 and k_{-1}, i.e., taking account of diffusion motion does not reduce to redefinition of the corresponding reaction constants according to the recipe for irreversible reaction in full agreement with the encounter theory notions. Just because of such a dependence, the kinetic principle of detailed balance is satisfied,[17] according to which the equilibrium constant

$$K_{eq} = \frac{[A_2]_{eq}[B_2]_{eq}}{[A_1]_{eq}[B_1]_{eq}} = \frac{k_{11}}{k_{12}} = \frac{k_{21}}{k_{22}} = \frac{k_{11}}{k_{22}} \equiv \frac{k_1}{k_{-1}} \quad (2.40)$$

is equal to reaction constants ratio independent of reactant mobility. So, to avoid misunderstanding, we shall call constants k_{11} and k_{22} as in Ref. 17 rate constants of forward and back transition channels of reversible reaction, respectively. It is readily seen that calculation of, for example, forward transition channel rate constant (neglecting back transition channel) corresponds to a simple kinetic scheme

$$A_1 + B_1 \underset{1/\tau_{c1}}{\overset{k_{d1}}{\rightleftarrows}} A_1 \ldots B_1 \underset{\langle w_{-1}(q) \rangle}{\overset{\langle w_1(q) \rangle}{\rightleftarrows}} A_2 \ldots B_2 \overset{1/\tau_{c2}}{\longrightarrow} A_2 + B_2, \quad (2.41)$$

excluding the encounter of reactants A_2 and B_2 ($k_{d2} \equiv 0$), not back reaction in the "cage." Note that formally putting $k_{d2} \equiv 0$, we take $^1/_{\tau_{c2}} \neq 0$. Thus, diffusion constant $k_{d2} = \frac{v_2}{\tau_{c2}}$ appearing in the rate constant k_{11} (2.38) or the efficiency p_1 (2.39) of forward channel is, of course, nonzero and corresponds to diffusion constant of "going out" from the state $A_2 \ldots B_2$ of the "cage complex" to the state of free walks of reactants A_2 and B_2. Thus, in calculations of forward transition channel efficiency, diffusion constant of "coming into" this state of the "cage complex" due to the encounter of reactants A_2 and B_2 in solution is formally put equal to zero, in full agreement with kinetic scheme (2.41) of the forward transition channel. Kinetic equations corresponding

to scheme (2.41) (i.e., at $k_{d2} \equiv 0$) yield Eq. (2.15) with $k_{12} = k_{22} \equiv 0$ describing concentration variation determined solely by forward transition channel of the reversible reaction under study. Similar examination is also performed in considering back transition channel. Note that derived expressions (2.38) show that reversible reaction can proceed in the kinetic regime (by any of the channels) only in the case where both forward and back reactions are kinetically controlled, i.e., if

$$k_1 \ll k_{d1_1} \quad \text{and} \quad k_{-1} \ll k_{d2}. \quad (2.42)$$

Then, reversible reaction becomes kinetically controlled by both channels, i.e., $k_{11} \approx k_1$ and $k_{22} \approx k_{-1}$.

As for diffusion control of reversible reaction, efficiencies p_1 and p_{-1} (2.39) depend essentially on whether forward reaction ($k_1 \gg k_{d1}$) or back one ($k_{-1} \gg k_{d2}$), or both are diffusion controlled. Unlike irreversible reaction, in the general case, the efficiency of diffusion controlled transition channel (either forward or back) does not become unity, but depends on the ratio of reaction constants of forward and back reactions (equilibrium constants (2.40)) and ratio of the corresponding diffusion constants. Instead of equality to unity of the efficiency of diffusion controlled irreversible reaction, in reversible reaction, the following relation takes place in the case of diffusion control of any of the channels (either forward or back, or both):

$$p_1 + p_{-1} \approx 1. \quad (2.43)$$

Thus, in reversible reaction, the presence of a "cage" at diffusion motion of reactants does not reduce to simple redefinition of rate constants of forward and back transition channels by the recipes typical of irreversible reactions.

III. TWO-STAGE REVERSIBLE BIMOLECULAR REACTIONS

A. Encounter theory

Now consider reversible two-stage consecutive reaction

$$A_1 + B_1 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A_2 + B_2 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} A_3 + B_3. \quad (3.1)$$
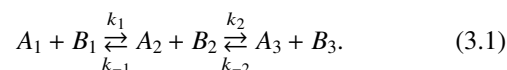
Equations of formal chemical kinetics of the reaction proceeding in the kinetic regime have the form

$$\frac{d[A_1]_t}{dt} = \frac{d[B_1]_t}{dt} = -k_1[A_1]_t[B_1]_t + k_{-1}[A_2]_t[B_2]_t,$$

$$\frac{d[A_2]_t}{dt} = \frac{d[B_2]_t}{dt} = k_1[A_1]_t[B_1]_t$$
$$- (k_{-1} + k_2)[A_2]_t[B_2]_t + k_{-2}[A_3]_t[B_3]_t, \quad (3.2)$$

$$\frac{d[A_3]_t}{dt} = \frac{d[B_3]_t}{dt} = k_2[A_2]_t[B_2]_t - k_{-2}[A_3]_t[B_3]_t.$$

As before, further the rebound effect will be neglected for simplicity. So we have the expressions for reaction constants in terms of elementary event rates $w_1(q)$, $w_{-1}(q)$, $w_2(q)$, $w_{-2}(q)$,

$$k_1 = \int w_1(q)\varphi_1(q)dq, \quad k_{-1} = \int w_{-1}(q)\varphi_2(q)dq,$$

$$k_2 = \int w_2(q)\varphi_2(q)dq, \quad k_{-2} = \int w_{-2}(q)\varphi_3(q)dq, \tag{3.3}$$

and the detailed balance principle for the rates

$$\frac{w_1(q)\varphi_1(q)}{k_1} = \frac{w_{-1}(q)\varphi_2(q)}{k_{-1}},$$

$$\frac{w_2(q)\varphi_2(q)}{k_2} = \frac{w_{-2}(q)\varphi_3(q)}{k_{-2}}. \tag{3.4}$$
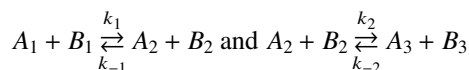
Here, $\varphi_1(q)$, $\varphi_2(q)$ and $\varphi_3(q)$ are stationary distributions in appropriate reaction channels. As earlier, introduce the normalized functions (shapes of the corresponding reaction zones) $\psi_1(q)$, $\psi_2(q)$, and $\psi_3(q)$ (see Eq. (2.7))

$$\psi_1(q) = \frac{w_1(q)}{k_1},$$

$$\psi_2(q) = \frac{w_{-1}(q)}{k_{-1}} \approx \frac{w_2(q)}{k_2} \approx \frac{w_{-1}(q) + w_2(q)}{k_{-1} + k_2}, \tag{3.5}$$

$$\psi_3(q) = \frac{w_{-2}(q)}{k_{-2}},$$

i.e., elementary transformation rates may be represented as

$$w_1(q) = k_1\psi_1(q), \ w_{-1}(q) = k_{-1}\psi_2(q),$$

$$w_2(q) = k_2\psi_2(q), \ w_{-2}(q) = k_{-2}\psi_3(q). \tag{3.6}$$

Note that the reaction zone shapes for back (transition to the first channel $A_1 + B_1$) and forward (transition to the third channel $A_3 + B_3$) reactions in the second channel $A_2 + B_2$ are put identical, and this is an additional requirement that does not follow from the detailed balance principle for rates (3.4). Physically, this means that reversible stages

$$A_1 + B_1 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A_2 + B_2 \text{ and } A_2 + B_2 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} A_3 + B_3$$

of the two-stage reaction in question proceed from one and the same reaction site at the encounters of reactants A_2 and B_2, as is usually assumed in the literature,[12,16] since, commonly, reactants with isotropic reactivity are considered. Such a restriction is necessary when just one state $A_2 \ldots B_2$ of the "cage complex" is taken into account for second channel, and this is assumed in this work.

However, it should be noted that another situation is more realistic, for example, for multistage biological reactions. It is the case where stages proceed from different sites the examination of which is possible in the framework of the encounter theory formalism used. However, this complicates consideration, and will be done elsewhere.

In view of Eqs. (3.4) and (3.5), we see that the relation takes place,

$$\psi_1(q)\varphi_1(q) = \psi_2(q)\varphi_2(q) = \psi_3(q)\varphi_3(q). \tag{3.7}$$

To obtain kinetic equations for this reaction with allowance for reactant motion in solution, we use Equations (2.12) and (2.13) of the encounter theory. According to the encounter theory, we introduce the column vectors $[\mathbf{A}]_t$ and $[\mathbf{B}]_t$ of concentrations with the components $[A_i]_t$ ($i = 1, 2, 3$), and $[B_k]_t$ ($k = 1, 2, 3$), elementary event rates, and motion operators matrices (Liouvillians) in the collective states basis (ik). The collective basis (ik) of two particles has nine states. However, taking into account that the reaction under study leads to transitions solely between collective states $(11) = I$, $(22) = II$ and $(33) = III$, consideration can be confined to such a restricted bases. Then, elementary event rates and motion operators' matrices (Liouvillians) in this collective states basis are

$$\hat{\mathbf{W}} = \begin{pmatrix} -w_1(q) & w_{-1}(q) & 0 \\ w_1(q) & -(w_{-1}(q) + w_2(q)) & w_{-2}(q) \\ 0 & w_2(q) & -w_{-2}(q) \end{pmatrix},$$

$$\hat{\mathbf{L}}_q = \begin{pmatrix} \hat{\mathcal{L}}_q^{(1)} & 0 & 0 \\ 0 & \hat{\mathcal{L}}_q^{(2)} & 0 \\ 0 & 0 & \hat{\mathcal{L}}_q^{(3)} \end{pmatrix}, \tag{3.8}$$

where $\hat{\mathcal{L}}_q^{(i)}$ ($i = 1, 2, 3$) are the relative motion operators in the corresponding channel.

Note that elementary event rates Liouvillian $\hat{\mathbf{W}}$ involve no matrix elements corresponding to chemical conversion of reactants of the first channel into reactants of the third channel in full agreement with kinetic equations (3.2) corresponding to the mechanism of consecutive two-stage reaction (3.1). Equations (3.2) correspond to reaction proceeding in the kinetic regime. Now let us see what we achieve by taking consistent account of reactants motion.

Let us introduce the notation for matrix elements of the Liouvillian $\hat{\mathbf{G}}(q)$,

$$\begin{array}{lll} G_{I\,I} = n_1 \equiv n_1^+(q)\varphi_1(q), & G_{I\,II} = m_2 \equiv m_2^+(q)\varphi_1(q), & G_{I\,III} = m_3 \equiv m_3^+(q)\varphi_1(q), \\ G_{II\,I} = m_1 \equiv m_1^+(q)\varphi_2(q), & G_{II\,II} = n_2 \equiv n_2^+(q)\varphi_2(q), & G_{II\,III} = l_3 \equiv l_3^+(q)\varphi_2(q), \\ G_{III\,I} = l_1 \equiv l_1^+(q)\varphi_3(q), & G_{III\,II} = l_2 \equiv l_2^+(q)\varphi_3(q), & G_{III\,III} = n_3 \equiv n_3^+(q)\varphi_3(q). \end{array} \tag{3.9}$$

Then, Equations (2.13) of the encounter theory take the form of three groups of equations relating elements (3.9) for different channels. The first group is

$$\frac{\partial}{\partial t}n_1(q,t) = -w_1(q)n_1(q,t) + w_{-1}(q)m_1(q,t) + \hat{\mathcal{L}}_q^{(1)}n_1(q,t),$$

$$\frac{\partial}{\partial t}m_1(q,t) = w_1(q)n_1(q,t) - (w_{-1}(q) + w_2(q))m_1(q,t) + w_{-2}(q)l_1(q,t) + \hat{\mathcal{L}}_q^{(2)}m_1(q,t), \tag{3.10a}$$

$$\frac{\partial}{\partial t}l_1(q,t) = w_2(q)m_1(q,t) - w_{-2}(q)l_1(q,t) + \hat{\mathcal{L}}_q^{(3)}l_1(q,t).$$

The second group is

$$\frac{\partial}{\partial t} m_2(q,t) = -w_1(q)\, m_2(q,t) + w_{-1}(q) n_2(q,t)$$
$$+ \hat{\mathcal{L}}_q^{(1)} m_2(q,t),$$

$$\frac{\partial}{\partial t} n_2(q,t) = w_1(q)\, m_2(q,t)$$
$$- (w_{-1}(q) + w_2(q))\, n_2(q,t)$$
$$+ w_{-2}(q) l_2(q,t) + \hat{\mathcal{L}}_q^{(2)} n_2(q,t),\quad (3.10b)$$

$$\frac{\partial}{\partial t} l_2(q,t) = w_2(q)\, n_2(q,t) - w_{-2}(q) l_2(q,t)$$
$$+ \hat{\mathcal{L}}_q^{(3)} l_2(q,t).$$

The third group is

$$\frac{\partial}{\partial t} m_3(q,t) = -w_1(q)\, m_3(q,t) + w_{-1}(q) l_3(q,t)$$
$$+ \hat{\mathcal{L}}_q^{(1)} m_3(q,t),$$

$$\frac{\partial}{\partial t} l_3(q,t) = w_1(q)\, m_3(q,t)$$
$$- (w_{-1}(q) + w_2(q))\, l_3(q,t)$$
$$+ w_{-2}(q) n_3(q,t) + \hat{\mathcal{L}}_q^{(2)} l_3(q,t),\quad (3.10c)$$

$$\frac{\partial}{\partial t} n_3(q,t) = w_2(q)\, l_3(q,t) - w_{-2}(q) n_3(q,t)$$
$$+ \hat{\mathcal{L}}_q^{(3)} n_3(q,t).$$

Now, just as in examining elementary reversible reaction, we introduce averaging of quantities (2.22) over reaction zones (3.5). By virtue of Eq. (3.7), the results of averaging over any of the three reaction zones coincide. Equation (2.12) of the encounter theory gives

$$\frac{d[A_1]_t}{dt} = \frac{d[B_1]_t}{dt}$$
$$= -k_{11}[A_1]_t[B_1]_t + k_{12}[A_2]_t[B_2]_t + k_{13}[A_3]_t[B_3]_t,$$

$$\frac{d[A_2]_t}{dt} = \frac{d[B_2]_t}{dt}$$
$$\quad (3.11)$$
$$= k_{21}[A_1]_t[B_1]_t - k_{22}[A_2]_t[B_2]_t + k_{23}[A_3]_t[B_3]_t,$$

$$\frac{d[A_3]_t}{dt} = \frac{d[B_3]_t}{dt}$$
$$= k_{31}[A_1]_t[B_1]_t + k_{32}[A_2]_t[B_2]_t - k_{33}[A_3]_t[B_3]_t,$$

where

$$k_{11} = k_{21} + k_{31} = k_1 \langle n_1^+(q) \rangle - k_{-1} \langle m_1^+(q) \rangle,$$
$$k_{21} = k_1 \langle n_1^+(q) \rangle - (k_{-1} + k_2) \langle m_1^+(q) \rangle$$
$$+ k_{-2} \langle l_1^+(q) \rangle,\quad (3.12a)$$
$$k_{31} = k_2 \langle m_1^+(q) \rangle - k_{-2} \langle l_1^+(q) \rangle;$$

$$k_{12} = k_{-1} \langle n_2^+(q) \rangle - k_1 \langle m_2^+(q) \rangle,$$
$$k_{22} = k_{12} + k_{32} = (k_{-1} + k_2) \langle n_2^+(q) \rangle$$
$$- k_1 \langle m_2^+(q) \rangle - k_{-2} \langle l_2^+(q) \rangle,\quad (3.12b)$$
$$k_{32} = k_2 \langle n_2^+(q) \rangle - k_{-2} \langle l_2^+(q) \rangle;$$

$$k_{13} = k_{-1} \langle l_3^+(q) \rangle - k_1 \langle m_3^+(q) \rangle,$$
$$k_{23} = k_1 \langle m_3^+(q) \rangle - (k_{-1} + k_2) \langle l_3^+(q) \rangle$$
$$+ k_{-2} \langle n_3^+(q) \rangle,\quad (3.12c)$$
$$k_{33} = k_{13} + k_{23} = k_{-2} \langle n_3^+(q) \rangle - k_2 \langle l_3^+(q) \rangle.$$

In view of definitions (3.12) of rate constants, Eqs. (3.11) immediately give the complete balance principle (preservation of the complete number of particles in the course of multistage reaction at hand).

Noteworthy is the fact that, unlike the reactions proceeding in the kinetic regime (see Eqs. (3.2)), taking into account reactant motion in solution results in that additional rate constants k_{31} and k_{13} appear in kinetic equations (3.11). This means the appearance of transitions between channels $A_1 + B_1$ and $A_3 + B_3$ (new transition channels) not directly related by the reaction interaction (see the reaction Liouvillian in Eq. (3.8) which involves no matrix elements between the first and the third states). So, taking into account the reactant motion in solution affects the mechanism of the two-stage reaction under study thus leading to mutual transformation of channels not connected by chemical interaction. This fact will be interpreted below.

Defining the corresponding reaction zone volumes, the mean residence times in the reaction zones for the starting position q[19,20] (2.23) ($i = 1, 2, 3$), and total residence time (2.28) ($i = 1, 2, 3$), and applying decoupling procedure (2.27) on conditions (2.29) ($i = 1, 2, 3$), as well as representations of form (2.24) for reaction constants

$$k_1 = \langle w_1(q) \rangle v_1, \qquad k_{-1} = \langle w_{-1}(q) \rangle v_2,$$
$$k_2 = \langle w_2(q) \rangle v_2, \qquad k_{-2} = \langle w_{-2}(q) \rangle v_3,\quad (3.13)$$

and the reaction rate constants in mobility controlled regime (2.30) ($i = 1, 2, 3$), we obtain from Eqs. (3.10a) in view of Eqs. (3.12a),

$$\langle n_1^+(q) \rangle = 1 - \frac{k_1}{k_{d1}} \langle n_1^+(q) \rangle + \frac{k_{-1}}{k_{d1}} \langle m_1^+(q) \rangle$$
$$\equiv 1 - \frac{k_{11}}{k_{d1}} = 1 - \frac{k_{21} + k_{31}}{k_{d1}},$$

$$\langle m_1^+(q) \rangle = \frac{k_1}{k_{d2}} \langle n_1^+(q) \rangle - \frac{k_{-1} + k_2}{k_{d2}} \langle m_1^+(q) \rangle$$
$$+ \frac{k_{-2}}{k_{d2}} \langle l_1^+(q) \rangle \equiv \frac{k_{21}}{k_{d2}},\quad (3.14a)$$

$$\langle l_1^+(q) \rangle = \frac{k_2}{k_{d3}} \langle m_1^+(q) \rangle - \frac{k_{-2}}{k_{d3}} \langle l_1^+(q) \rangle = \frac{k_{31}}{k_{d3}}.$$

Eqs. (3.10b), in view of Eqs. (3.12b), yield

$$\langle m_2^+(q) \rangle = -\frac{k_1}{k_{d1}} \langle m_2^+(q) \rangle + \frac{k_{-1}}{k_{d1}} \langle n_2^+(q) \rangle \equiv \frac{k_{12}}{k_{d1}},$$

$$\langle n_2^+(q) \rangle = 1 + \frac{k_1}{k_{d2}} \langle m_2^+(q) \rangle - \frac{k_{-1} + k_2}{k_{d2}} \langle n_2^+(q) \rangle$$
$$+ \frac{k_{-2}}{k_{d2}} \langle l_2^+(q) \rangle \equiv 1 - \frac{k_{22}}{k_{d2}} = 1 - \frac{k_{12} + k_{32}}{k_{d2}},$$

$$\langle l_2^+(q) \rangle = \frac{k_2}{k_{d3}} \langle n_2^+(q) \rangle - \frac{k_{-2}}{k_{d3}} \langle l_2^+(q) \rangle = \frac{k_{32}}{k_{d3}}.\quad (3.14b)$$

Eqs. (3.10c), in view of Eqs. (3.12c), give

$$\langle m_3^+(q) \rangle = -\frac{k_1}{k_{d1}} \langle m_3^+(q) \rangle + \frac{k_{-1}}{k_{d1}} \langle l_3^+(q) \rangle \equiv \frac{k_{13}}{k_{d1}},$$

$$\langle l_3^+(q) \rangle = \frac{k_1}{k_{d2}} \langle m_3^+(q) \rangle - \frac{k_{-1} + k_2}{k_{d2}} \langle l_3^+(q) \rangle$$
$$+ \frac{k_{-2}}{k_{d2}} \langle n_3^+(q) \rangle \equiv \frac{k_{23}}{k_{d2}}, \qquad (3.14c)$$

$$\langle n_3^+(q) \rangle = 1 + \frac{k_2}{k_{d3}} \langle l_3^+(q) \rangle - \frac{k_{-2}}{k_{d3}} \langle n_3^+(q) \rangle$$
$$\equiv 1 - \frac{k_{33}}{k_{d3}} = 1 - \frac{k_{13} + k_{23}}{k_{d3}}.$$

With Eqs. (3.12a), we derive from Eqs. (3.14a) a closed set of equations to find rate constants k_{21} and k_{31}, and, therefore, $k_{11} = k_{21} + k_{31}$. Accordingly, Eqs. (3.12b) and Eqs. (3.14b) yield a closed set of equation to determine rate constants k_{12} and k_{32}, and, therefore, $k_{22} = k_{12} + k_{32}$. From Eqs. (3.12c) and Eqs. (3.14c), we obtain a closed set of equations to find rate constants k_{13} and k_{23}, and, therefore, $k_{33} = k_{13} + k_{23}$. However, before giving these equations, we must check whether the

exact kinetic equations obtained by the encounter theory for reactions proceeding in a thin contact zone may be derived on the basis of a simple kinetic scheme relying on the concepts of the "cage complex."

B. The "cage complex" method

Let us introduce the "cage complex" states concentrations by the rule given in the consideration of elementary reversible reaction. By this rule, each state involves quantities from different sets of equations ($i = 1, 2, 3$), and this corresponds to Eqs. (3.10a)–(3.10c) (or Eqs. (3.14a)–(3.14c)). As it must be, the "cage complex" $A_i \ldots B_i$ includes the averaged pair densities, the motion of which is described by the operator $\hat{\mathcal{L}}_q^{(i)}$ of the initial pair of reactants (or adjoint pair densities obtained from initial ones by division by the corresponding stationary distributions $\varphi_i(q)$). Quantities from the ith system are multiplied by concentrations product $[A_i]_t[B_i]_t$ of the ith reaction channel. Thus, the "cage complex" states concentrations are

$$[A_1 \ldots B_1] = \upsilon_1 \left(\langle n_1^+(q) \rangle [A_1]_t[B_1]_t + \langle m_2^+(q) \rangle [A_2]_t[B_2]_t + \langle m_3^+(q) \rangle [A_3]_t[B_3]_t \right),$$
$$[A_2 \ldots B_2] = \upsilon_2 \left(\langle m_1^+(q) \rangle [A_1]_t[B_1]_t + \langle n_2^+(q) \rangle [A_2]_t[B_2]_t + \langle l_3^+(q) \rangle [A_3]_t[B_3]_t \right), \qquad (3.15)$$
$$[A_3 \ldots B_3] = \upsilon_3 \left(\langle l_1^+(q) \rangle [A_1]_t[B_1]_t + \langle l_2^+(q) \rangle [A_2]_t[B_2]_t + \langle n_3^+(q) \rangle [A_3]_t[B_3]_t \right).$$
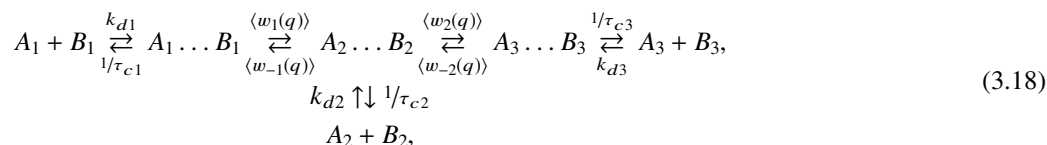
With these quantities, Eqs. (3.11), in view of Eqs. (2.30) and (3.14), may be written as

$$\frac{d[A_1]_t}{dt} = \frac{d[B_1]_t}{dt} = -k_{d1}[A_1]_t[B_1]_t + \frac{1}{\tau_{c1}}[A_1 \ldots B_1],$$

$$\frac{d[A_2]_t}{dt} = \frac{d[B_2]_t}{dt} = -k_{d2}[A_2]_t[B_2]_t + \frac{1}{\tau_{c2}}[A_2 \ldots B_2], \qquad (3.16)$$

$$\frac{d[A_3]_t}{dt} = \frac{d[B_3]_t}{dt} = -k_{d3}[A_3]_t[B_3]_t + \frac{1}{\tau_{c3}}[A_3 \ldots B_3].$$

As is easily shown using Eqs. (3.15) and (3.14), the quantities themselves satisfy the set of equations that can be treated as equations for quasi-stationary concentrations of states of the "cage complex,"

$$\frac{d}{dt}[A_1 \ldots B_1]_t \approx 0 = k_{d1}[A_1]_t[B_1]_t - (\langle w_1(q) \rangle + 1/\tau_{c1})[A_1 \ldots B_1]_t + \langle w_{-1}(q) \rangle [A_2 \ldots B_2]_t,$$

$$\frac{d}{dt}[A_2 \ldots B_2]_t \approx 0 = k_{d2}[A_2]_t[B_2]_t + \langle w_1(q) \rangle [A_1 \ldots B_1]_t$$
$$- (\langle w_{-1}(q) \rangle + \langle w_2(q) \rangle + 1/\tau_{c2})[A_2 \ldots B_2]_t + \langle w_{-2}(q) \rangle [A_3 \ldots B_3]_t, \qquad (3.17)$$

$$\frac{d}{dt}[A_3 \ldots B_3]_t \approx 0 = k_{d3}[A_3]_t[B_3]_t + \langle w_2(q) \rangle [A_2 \ldots B_2]_t - (\langle w_{-2}(q) \rangle + 1/\tau_{c3})[A_3 \ldots B_3]_t.$$

Eqs. (3.16) and (3.17) correspond to equations of formal chemical kinetics for a simple kinetic scheme

$$A_1 + B_1 \underset{1/\tau_{c1}}{\overset{k_{d1}}{\rightleftarrows}} A_1 \ldots B_1 \underset{\langle w_{-1}(q) \rangle}{\overset{\langle w_1(q) \rangle}{\rightleftarrows}} A_2 \ldots B_2 \underset{\langle w_{-2}(q) \rangle}{\overset{\langle w_2(q) \rangle}{\rightleftarrows}} A_3 \ldots B_3 \underset{k_{d3}}{\overset{1/\tau_{c3}}{\rightleftarrows}} A_3 + B_3,$$
$$k_{d2} \uparrow\downarrow 1/\tau_{c2} \qquad (3.18)$$
$$A_2 + B_2,$$

which differs from the scheme for irreversible two-stage consecutive reaction[15] only in the presence of back transitions between the corresponding states of the "cage complex." This fact does not affect the form of kinetic equations (3.16) and just slightly complicates Eqs. (3.17) now describing reversible transition between successive states of the "cage complex." As in the case of elementary reversible reaction, calculation of rate constants of the reaction in question is easier to do on the basis of Eqs. (3.14)

of the encounter theory. However, representation of kinetic scheme (3.18) in the form of kinetic equations (3.16) and (3.17) is useful to chemical community from the standpoint of clear chemical interpretation of the results derived.

Calculation of rate constants gives the expressions that are conveniently represented by introducing, in full agreement with Eqs. (2.38) and (2.39), rate constants and efficiencies (denoted by upper indices (1) or (2)) of each of the reversible elementary stages of the reaction, i.e., for reversible transition channels $A_1 + B_1 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A_2 + B_2$ and $A_2 + B_2 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} A_3 + B_3$, respectively,

$$k_{21}^{(1)} = k_{d1}p_1, \qquad k_{12}^{(1)} = k_{d2}p_{-1}, \qquad k_{32}^{(2)} = k_{d2}p_2, \qquad k_{23}^{(2)} = k_{d3}p_{-2}, \tag{3.19}$$

where, along with the efficiencies of forward and back reactions at the first stage p_1 and p_{-1} (2.39), the efficiencies of forward and back reactions at the second stage are introduced

$$p_2 = \frac{k_2/k_{d2}}{1 + k_2/k_{d2} + k_{-2}/k_{d3}}, \qquad p_{-2,} = \frac{k_{-2}/k_{d3}}{1 + k_2/k_{d2} + k_{-2}/k_{d3}}. \tag{3.20}$$

Expressions for rate constants in Eqs. (3.11) calculated by the encounter theory or equations of formal kinetic scheme may be represented in the form of kinetic coefficient matrix

$$\mathbf{K} = \begin{pmatrix} -k_{11} & k_{12} & k_{13} \\ k_{21} & -k_{22} & k_{23} \\ k_{31} & k_{32} & -k_{33} \end{pmatrix} = \begin{pmatrix} -k_{21}^{(1)}\dfrac{1}{1-p_{-1}p_2} & k_{12}^{(1)}\dfrac{1-p_2}{1-p_{-1}p_2} & k_{23}^{(2)}\dfrac{p_{-1}}{1-p_{-1}p_2} \\ k_{21}^{(1)}\dfrac{1-p_2}{1-p_{-1}p_2} & -k_{12}^{(1)}\dfrac{1-p_2}{1-p_{-1}p_2} - k_{32}^{(2)}\dfrac{1-p_{-1}}{1-p_{-1}p_2} & k_{23}^{(2)}\dfrac{1-p_{-1}}{1-p_{-1}p_2} \\ k_{21}^{(1)}\dfrac{p_2}{1-p_{-1}p_2} & k_{32}^{(2)}\dfrac{1-p_{-1}}{1-p_{-1}p_2} & -k_{23}^{(2)}\dfrac{1}{1-p_{-1}p_2} \end{pmatrix}, \tag{3.21a}$$

or, using expressions (3.19), as

$$\mathbf{K} = \begin{pmatrix} -k_{d1}\dfrac{p_1}{1-p_{-1}p_2} & k_{d2}\dfrac{p_{-1}(1-p_2)}{1-p_{-1}p_2} & k_{d3}\dfrac{p_{-2}p_{-1}}{1-p_{-1}p_2} \\ k_{d1}\dfrac{p_1(1-p_2)}{1-p_{-1}p_2} & -k_{d2}\dfrac{p_{-1}(1-p_2)+p_2(1-p_{-1})}{1-p_{-1}p_2} & k_{d3}\dfrac{p_{-2}(1-p_{-1})}{1-p_{-1}p_2} \\ k_{d1}\dfrac{p_1p_2}{1-p_{-1}p_2} & k_{d2}\dfrac{p_2(1-p_{-1})}{1-p_{-1}p_2} & -k_{d3}\dfrac{p_{-2}}{1-p_{-1}p_2} \end{pmatrix}. \tag{3.21b}$$

Of course, the derived rate constants satisfy the relations expressing material balance (preservation of total concentration of reactants A_i и $B_i (i = 1, 2, 3)$) and the detailed balance principle providing correct values of equilibrium concentrations (note that only in this case the obtained equations may be considered as kinetic),

$$k_{11} = k_{21} + k_{31}, \quad k_{22} = k_{12} + k_{32}, \quad k_{33} = k_{13} + k_{23} \tag{3.22}$$

and

$$K_{eq}^{(1)} = \frac{k_{21}}{k_{12}} = \frac{k_1}{k_{-1}}, \qquad K_{eq}^{(2)} = \frac{k_{32}}{k_{23}} = \frac{k_2}{k_{-2}},$$
$$K_{eq} = K_{eq}^{(1)}K_{eq}^{(2)} = \frac{k_{31}}{k_{13}} = \frac{k_1 k_2}{k_{-1}k_{-2}}, \tag{3.23}$$

where

$$\frac{[A_2]_{eq}[B_2]_{eq}}{[A_1]_{eq}[B_1]_{eq}} = K_{eq}^{(1)}, \qquad \frac{[A_3]_{eq}[B_3]_{eq}}{[A_2]_{eq}[B_2]_{eq}} = K_{eq}^{(2)},$$
$$\frac{[A_3]_{eq}[B_3]_{eq}}{[A_1]_{eq}[B_1]_{eq}} = K_{eq} \tag{3.24}$$

are equilibrium constants ($[A_i]_{eq}$ и $[B_i]_{eq}$ $(i = 1, 2, 3)$—equilibrium concentrations).

C. Mechanisms of reversible two-stage reaction

Comparison between Eqs. (3.2) and (3.21) shows that, as in irreversible reactions,[15] diffusion "cage effect" results in redefinition of kinetic constants of each of the elementary reversible stages. However, in contrast to irreversible reaction, where rate constants k_{11} and $k_{32} = k_{22}$ of the reaction of each stage are equal to the corresponding rate constants in appropriate one-stage reaction (see Eqs. (3.21) at $p_{-1} = p_{-2} \equiv 0$), in reversible reaction, the constants are redefined in a more complicated way than in one-stage reversible reaction. However, it is more interesting that, unlike three-diagonal rate constant (reaction constant) matrix of Eq. (3.2),

$$\mathbf{K} = \begin{pmatrix} -k_1 & k_{-1} & 0 \\ k_1 & -(k_{-1}+k_2) & k_{-2} \\ 0 & k_2 & -k_{-2} \end{pmatrix}, \tag{3.25}$$

taking place at kinetic reaction control, matrices (3.21) are complete. This means that, as in the case of irreversible two-stage reaction, the "cage effect" gives rise to new transition channels of reversible transition between channels I and III, though such a direct transformation due to elementary event of chemical conversion is impossible for the given mechanism

of consecutive two-stage chemical reaction. Rate constants of new transition channels (forward and back) are as follows:

$$k_{13} = k_{23}^{(2)} \frac{p_{-1}}{1 - p_{-1} p_2} = k_{d3} \frac{p_{-2} \, p_{-1}}{1 - p_{-1} p_2},$$
$$k_{31} = k_{21}^{(1)} \frac{p_2}{1 - p_{-1} p_2} = k_{d1} \frac{p_1 \, p_2}{1 - p_{-1} p_2}. \tag{3.26}$$

The appearance of these new transition channels drastically affecting the mechanism of the reaction course (a set of kinetic equations of formal chemical kinetics based on the kinetic law of mass action) is easily interpreted both in the framework of the encounter theory, and in the concepts of the "cage complex" method. In the encounter theory, for example, this is explained by the fact that reactants A_1 and B_1 which encountered in solution, during the encounter time (residence in the "cage"), are consistently transformed into reactants A_2 and B_2 that are subsequently transformed into reactants A_3 and B_3. Thus, the encounter of reactants A_1 and B_1 results in reactants A_3 and B_3. In the "cage complex" method, the appearance of additional transition channels is explained by the fact that, according to Eq. (3.17), in the "cage complex" transitions between any of its states are possible including states $A_1 \ldots B_1$ and $A_3 \ldots B_3$.

In the case of kinetic reaction control at both stages $p_i \ll 1$ ($i = 1, -1, 2, -2$), or $k_1 \ll k_{d1}$; k_{-1}, $k_2 \ll k_{d2}$; $k_{-2} \ll k_{d3}$, these constants go to zero (at small but finite values p_i these rate constants are the values of the next order of smallness as compared to reaction constants), and the obtained matrix reduces to reaction constant matrix (3.25) in Eqs. (3.2).

If only the second stage is kinetically controlled, i.e., $k_2 \ll k_{d2}, k_{-2} \ll k_{d3}$, or $p_2 \approx k_2/k_{d2} \ll 1$, $p_{-2} \approx k_{-2}/k_{d3} \ll 1$, kinetic coefficient matrix (3.21a) takes the form

$$\mathbf{K} = \begin{pmatrix} -k_{21}^{(1)} & k_{12} & k_{-2} \, p_{-1} \\ k_{21}^{(1)}(1 - p_2) & -k_{12} - k_2 (1 - p_{-1}) & k_{-2}(1 - p_{-1}) \\ k_{21}^{(1)} p_2 & k_2 (1 - p_{-1}) & -k_{-2} \end{pmatrix}, \tag{3.27}$$

i.e., rate constants k_{13} and k_{31} of new transition channels are not small as compared to reaction constants k_2 and k_{-2} at the second stage, though they are small in comparison with rate constants $k_{11} = k_{21} \approx k_{21}^{(1)}$, since

$$k_{31} \approx k_{21}^{(1)} p_2 \approx \frac{k_1}{k_{-1}} k_2 \, p_{-1}$$
$$= K_{eq} \, k_{-2} \, p_{-1} \ll k_{21}^{(1)} \, (p_2 \ll 1). \tag{3.28}$$

As in irreversible two-stage reaction,[15] the efficiency of new transition channels increases monotonically with increasing efficiencies p_{-1} and p_2 of reactant transformation in the second channel (A_2 and B_2) (due to "going out" of the cage complex from the intermediate state $A_2 \ldots B_2$).

Consider the limiting case $p_{-1} \to 1$, $p_2 \to 1$ corresponding to diffusion controlled transition reactions from the second channel to the first and the third channels, respectively. Note that at such a limiting transition, according to Eq. (2.43), $p_1 \to 0$, $p_{-2} \to 0$ (or $K_{eq}^{(1)} \to 0$, $K_{eq}^{(2)} \to \infty$), and this formally corresponds to the disappearance of transitions from the first channel to the second one and from the third channel to the second channel. However, in expressions (3.21b) at

$k_{-1}/k_{d2} \to \infty$ and $k_2/k_{d2} \to \infty$ with allowance for Eqs. (2.39) and (3.20) and fixing the values

$$K_{eq} = K_{eq}^{(1)} K_{eq}^{(2)} = \frac{k_1 k_2}{k_{-1} k_{-2}}$$
$$\equiv \alpha \frac{k_1}{k_{-2}} \quad \text{where} \quad \alpha = \frac{k_2}{k_{-1}}, \tag{3.29}$$

we obtain the matrix of kinetic coefficients corresponding to the kinetic equations

$$\frac{d[A_1]_t}{dt} = \frac{d[B_1]_t}{dt} = -k_f [A_1]_t [B_1]_t + k_{12} [A_2]_t [B_2]_t + k_r [A_3]_t [B_3]_t,$$
$$\frac{d[A_2]_t}{dt} = \frac{d[B_2]_t}{dt} = -k_{d2} [A_2]_t [B_2]_t, \tag{3.30}$$
$$\frac{d[A_3]_t}{dt} = \frac{d[B_3]_t}{dt} = k_f [A_1]_t [B_1]_t + k_{32} [A_2]_t [B_2]_t - k_r [A_3]_t [B_3]_t,$$

where

$$k_f = k_1 \alpha Z, \quad k_r = k_{-2} Z, \quad k_{12} = k_{d2} \left(1 + \frac{k_{-2}}{k_{d3}} \right) Z,$$
$$k_{32} = k_{d2} \left(1 + \frac{k_1}{k_{d1}} \right) Z \alpha, \tag{3.31}$$
$$\frac{1}{Z} = 1 + \frac{k_{-2}}{k_{d3}} + \left(1 + \frac{k_1}{k_{d1}} \right) \alpha.$$

If at the initial instant of time reactants A_2 or B_2 are absent in solution ($[A_2]_0 = 0$ or $[B_2]_0 = 0$), then they are not formed in the bulk ($[A_2]_t = 0$ or $[B_2]_t = 0$) despite the presence of reversible chemical transformations of reactants $A_1 + B_1$ and reactants $A_3 + B_3$ into reactants $A_2 + B_2$ in the "cage" (at encounters). Similar situation also took place in irreversible two-stage reaction at diffusion control of the second stage.[15] In the case at hand, reversible chemical transformation occurs between the first and the third channels with rate constants k_f and k_r of forward and back transient channels, respectively,

$$\frac{d[A_1]_t}{dt} = -k_f [A_1]_t [B_1]_t + k_r [A_3]_t [B_3]_t,$$
$$\frac{d[A_3]_t}{dt} = k_f [A_1]_t [B_1]_t - k_r [A_3]_t [B_3]_t, \tag{3.32}$$

i.e., formally corresponds to one-stage reversible reaction

$$A_1 + B_1 \underset{k_r}{\overset{k_f}{\rightleftarrows}} A_3 + B_3. \tag{3.33}$$
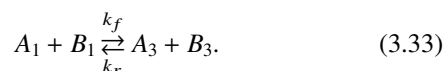
It is interesting that if forward reaction at the first stage and back reaction at the second stage of initial two-stage reaction proceed in the kinetic regime ($k_1 \ll k_{d1}$, $k_{-2} \ll k_{d3}$), then rate constants differ from the corresponding kinetic constants in that they include numerical factors depending on the value α,

$$k_f = k_1 \frac{\alpha}{1 + \alpha},$$
$$k_r = k_{-2} \frac{1}{1 + \alpha} \quad \left(\frac{k_f}{k_r} = \alpha \frac{k_1}{k_{-2}} = K_{eq} \right). \tag{3.34a}$$

At diffusion control of these reactions ($k_1 \gg k_{d1}$, $k_{-2} \gg k_{d3}$), rate constants differ from the corresponding diffusion constants in that they involve numerical factors depending on the ratio between diffusion constants and equilibrium constant

K_{eq},

$$k_f = k_{d1} \frac{K_{eq}}{\frac{k_{d1}}{k_{d3}} + K_{eq}},$$

$$k_r = k_{d3} \frac{1}{1 + \frac{k_{d3}}{k_{d1}} K_{eq}} \quad \left(\frac{k_f}{k_r} = K_{eq} \right). \tag{3.34b}$$

The appearance of these numerical factors in Eqs. (3.34) ensures the fulfillment of the detailed balance principle.

IV. MULTI-STAGE REVERSIBLE BIMOLECULAR REACTIONS

A. Encounter theory

In this section, we generalize the obtained results to arbitrary multistage reaction involving reversible exchange bimolecular reactions between nonidentical reactants as elementary stages. Since, as before, the reaction channel includes just a restricted basis of "diagonal" collective states $(i\,i) = I$, $(k\,k) = K$, channels can be numbered by small Latin letters. Let us introduce elementary rates $w_{ki}(q)$ of chemical transformation of reactants of the ith channel $(A_i + B_i)$ into reactants of the kth channel $(A_k + B_k)$, and $w_{ii}(q) = w_{kk}(q) \equiv 0$. Then, matrix elements of Liouvillian in Eqs. (2.12) and (2.13) of the elementary rates of such a transformation are

$$\left(\hat{\mathbf{W}} \right)_{ki} = - \sum_l w_{li}(q)\, \delta_{ki} + w_{ki}(q) \quad \left(\sum_k \left(\hat{\mathbf{W}} \right)_{ki} = 0 \right). \tag{4.1}$$

Diagonal elements of this Liouvillian are negative and describe going out of the kth channel, while positive nondiagonal elements define the rate of the corresponding transition channel $i \to k$. The Liouvillian $\hat{\mathbf{L}}_q$ in Eq. (2.13) is diagonal, and its matrix elements $\hat{\mathcal{L}}_q^{(k)}$ ($k = 1, 2, \ldots, N$) describe relative stochastic motion of reactants in appropriate channel. Now introduce the reaction constants of the transition channels

$$k_{ki}^0 = \int w_{ki}(q)\varphi_i(q)\, dq \quad (i, k = 1, 2, \ldots, N), \tag{4.2}$$

where $\varphi_i(q)$ is the stationary distribution in the ith reaction channel. We have the detailed balance principle for the rates

$$\frac{w_{ki}(q)\varphi_i(q)}{k_{ki}^0} = \frac{w_{ik}(q)\varphi_k(q)}{k_{ik}^0} \quad (i, k = 1, 2, \ldots, N). \tag{4.3}$$

Kinetic equations of formal chemical kinetics for multistage reaction proceeding in the kinetic regime are of the form

$$\frac{d\,[A_i]_t}{dt} = \frac{d\,[B_i]_t}{dt}$$
$$= - \sum_l k_{li}^0 [A_i]_t [B_i]_t + \sum_k k_{ik}^0\, [A_k]_t [B_k]_t. \tag{4.4}$$

As earlier, we introduce the normalized functions (shapes of the corresponding reaction zones) $\psi_i(q)$ (see Eqs. (2.7)-(2.9)),

$$\psi_i(q) \approx \psi_{ki}(q) = \frac{w_{ki}(q)}{k_{ki}^0} \approx \frac{\sum_k w_{ki}(q)}{\sum_k k_{ki}^0},$$

$$w_{ki}(q) \approx k_{ki}^0 \psi_i(q). \tag{4.5}$$

Note that, as in Sec. III, the reaction zone shapes for transitions from the given reaction channel to all other possible channels are put identical. This means that the reaction zone shape for the given channel is one and the same whatever the number of transitions to other channels. As in Eq. (3.5), this is an additional requirement not following from the detailed balance principle. Such a restriction is necessary in taking into consideration just one state $A_i \ldots B_i$ of the "cage complex" in the ith channels of multistage reaction, and this is assumed in the present work.

Then, in view of detailed balance principle (4.3), we have

$$\psi_i(q)\varphi_i(q) = \psi_k(q)\, \varphi_k(q) \quad (i, k = 1, 2, \ldots N). \tag{4.6}$$

If the rate of chemical transformations in the multistage reaction is essential, then the reaction course will be affected by the process of the approach of reactants in solution, i.e., by their motion (commonly treated as continual diffusion). In this case, examination may only be based on Eqs. (2.12) and (2.13) of the encounter theory which give

$$\frac{d\,[A_i]_t}{dt} = \frac{d\,[B_i]_t}{dt} = \sum_{lk} \int \left(- \sum_m w_{mi}(q)\, \delta_{il} + w_{il}(q) \right)$$
$$\times G_{lk}(q)\, dq\, [A_k]_t [B_k]_t$$
$$\equiv -k_{ii}[A_i]_t [B_i]_t + \sum_k k_{ik}[A_k]_t [B_k]_t. \tag{4.7}$$

The steady-state Liouvillian of pair densities is the stationary solution $\hat{\mathbf{G}}(q) = \lim\limits_{t \to \infty} \hat{\mathbf{G}}(q, t)$ of the matrix equation

$$\frac{\partial}{\partial t} G_{ik}(q, t) = - \sum_m w_{mi}(q)\, G_{ik}(q, t)$$
$$+ \sum_l w_{il}(q) G_{lk}(q, t) + \hat{\mathcal{L}}_q^{(i)} G_{ik}(q, t). \tag{4.8}$$

Introducing, as before, averaging (see Eq. (2.22)) over the reaction zones $\psi_i(q)$ of stationary adjoint quantities $h_{ik}^+(q)$,

$$G_{ik}(q, t) \equiv h_{ik}^+(q)\, \varphi_i(q) \tag{4.9}$$

and taking into account Eqs. (4.5)–(4.7) ($i = 1, 2, \ldots, N$), we arrive at

$$k_{ii} = \sum_m k_{mi}^0 \langle h_{ii}^+(q) \rangle - \sum_l k_{il}^0 \langle h_{li}^+(q) \rangle,$$
$$k_{ki} = \sum_l k_{kl}^0 \langle h_{li}^+(q) \rangle - \sum_m k_{mk}^0 \langle h_{ki}^+(q) \rangle \quad (k \neq i). \tag{4.10}$$

As is readily seen, the equality takes place ensuring the fulfillment of the complete balance principle

$$k_{ii} = \sum_{k \neq i} k_{ki}. \tag{4.11}$$

Representing stationary $\left(\frac{\partial}{\partial t} G_{ik}(q, t) = 0 \right)$ form of Eq. (4.8) in the integral form, using Eqs. (4.5), (4.6), (2.23), (2.28), and (2.30) ($i = 1, 2, \ldots, N$), as well as the decoupling procedure of (2.27) type (under conditions of type (2.29)), we obtain the equations for quantities $\langle h_{li}^+(q) \rangle$

$$\langle h_{ii}^+(q)\rangle = 1 - \frac{1}{k_{di}}\sum_m k_{mi}^0(q)\,\langle h_{ii}^+(q)\rangle$$

$$+ \frac{1}{k_{di}}\sum_l k_{il}^0\,\langle h_{li}^+(q)\rangle$$

$$\equiv 1 - \frac{k_{ii}}{k_{di}} = 1 - \frac{1}{k_{di}}\sum_{k\neq i} k_{ki}, \qquad (4.12)$$

$$\langle h_{ki}^+(q)\rangle = -\frac{1}{k_{dk}}\sum_m k_{mk}^0\,\langle h_{ki}^+(q)\rangle$$

$$+ \frac{1}{k_{dk}}\sum_l k_{kl}^0\,\langle h_{li}^+(q)\rangle \equiv \frac{k_{ki}}{k_{dk}}\ (k\neq i).$$

With the second equalities from Eqs. (4.12) in the second Eq. (4.10), we derive the set of $N-1$ equations to find the values k_{ki} $(k\neq i)$,

$$\left(1 + \frac{k_{ki}^0}{k_{di}} + \frac{1}{k_{dk}}\sum_m k_{mk}^0\right) k_{ki} + \sum_{l\neq k}\left(\frac{k_{ki}^0}{k_{di}} - \frac{k_{kl}^0}{k_{dl}}\right) k_{li} = k_{ki}^0.$$

$$(4.13)$$

This set of equations yield sets of equations for the determination of rate constants for reactions studied in Secs. II and III. In the general case of consecutive multistage (containing N channels ($N-1$ stages)) reversible reaction in the kinetic regime, there are $N(N+1)/2$ rate constants. In diffusion influenced reaction, there are N^2 rate constants, i.e., $N(N-1)/2$ new transition channels appear.

It should be noted that in many-particle approach to the calculation of kinetics of reactions (including multistage ones) suggested in the literature,[23] it was proposed that the Markovian constants (corresponding to the kinetic regime of the reaction course) should be replaced by the corresponding diffusion-influenced reaction rate constants. These constants should be determined either by self-consistent procedure, or using the Markovian rate constants of elementary stages. In accordance with the results of the present work, the proposed approach can be employed solely in studies of elementary reversible reactions. For multistage reactions, it should be corrected.

B. The "cage complex" method

Now let us show that the multistage reaction containing reversible bimolecular exchange reactions between nonidentical reactants as elementary stages may be considered on the basis of formal kinetic scheme relying on the concepts of the "cage" complex. Introduce the "cage" complex concentrations by the rules given in examining elementary and consecutive two-stage reversible reactions,

$$[A_i\ldots B_i] = \upsilon_i \sum_l \langle h_{il}^+(q)\rangle\,[A_l]_t[B_l]_t. \qquad (4.14)$$

Then, the kinetic equations (the second equation in Eq. (4.7)), with the second equalities in Eqs. (4.12) and (2.30) $(i=1,2,\ldots,N)$ taken into account, may be recast as

$$\frac{d[A_i]_t}{dt} = \frac{d[B_i]_t}{dt} = -k_{di}[A_i]_t[B_i]_t$$

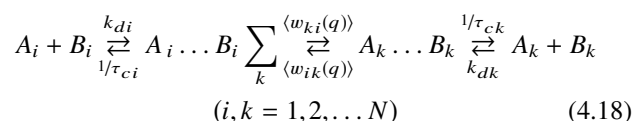$$+ \frac{1}{\tau_{ci}}[A_i\ldots B_i]\ (i=1,2,\ldots,N). \qquad (4.15)$$

In view of representation similar to Eqs. (2.24) and (3.13),

$$k_{ki}^0 = \langle w_{ki}(q)\rangle\,\upsilon_i \quad (i,k=1,2,\ldots,N). \qquad (4.16)$$

Quasistationary concentration $[A_i\ldots B_i]_t$ of the complex obeys the equation

$$\frac{d}{dt}[A_i\ldots B_i]_t \approx 0 = k_{di}[A_i]_t[B_i]_t$$

$$- \left(\sum_m \langle w_{mi}(q)\rangle + {}^1\!/\tau_{ci}\right)[A_i\ldots B_i]_t$$

$$+ \sum_k \langle w_{ik}(q)\rangle\,[A_k\ldots B_k]_t. \qquad (4.17)$$

This can easily be shown using expressions Eq. (4.14) of quasistationary concentrations of the "cage" complexes in terms of $\langle h_{il}^+(q)\rangle$ in Eq. (4.17). Equating the terms at equal values $[A_l]_t[B_l]_t$ $(i=1,2,\ldots N)$, we obtain Eq. (4.12). The above Equations (4.15) and (4.17) (in view of Eqs. (2.30) and (4.16)) correspond completely to the "cage complex" method based on the consideration of formal chemical kinetics equations for the following scheme:

$$A_i + B_i \underset{{}^1\!/\tau_{ci}}{\overset{k_{di}}{\rightleftarrows}} A_i\ldots B_i \sum_k \underset{\langle w_{ik}(q)\rangle}{\overset{\langle w_{ki}(q)\rangle}{\rightleftarrows}} A_k\ldots B_k \underset{k_{dk}}{\overset{{}^1\!/\tau_{ck}}{\rightleftarrows}} A_k + B_k$$

$$(i,k=1,2,\ldots N) \qquad (4.18)$$

under the assumption of quasi-stationary concentration of the cage complex. Note that conventional designation by introducing the summation symbol in Eq. (4.18) means that at any fixed value of the index i $(i=1,2,\ldots,N)$ the reaction transition from this state of the complex is realized to any other possible states $k\neq i$ $(k=1,2,\ldots,N)$, just as back reaction transitions from any state k $(k=1,2,\ldots,N)$ to the given state $i\neq k$ $(i=1,2,\ldots,N)$.

V. SUMMARY

Assuming that any elementary reversible reaction in any reaction channel proceeds from one and the same reaction site, it is shown that the "cage complex" method (the method of quasi-stationary concentrations of "collision" complex in equations of formal chemical kinetics) is in full agreement with the concepts of the encounter theory which is the analog of semi-classical gas collision theory. However, there is fundamental difference between collisions of reactants in gases and encounters (residence in the "cage") of reactants in liquid solutions. Collision time distribution in gases is Poisson, and encounter time distribution (encounter is a combination of re-contacts) is not.

However, application the "cage complex" method to the consideration of elementary reversible reaction leads to the result corresponding to the exponential model. This is because by the "cage complex," we imply not the entire encounter of reactants but just a part of it, when reactants are in contact that results in elementary event of chemical transformation. In the absence of physicochemical processes between re-contacts, the efficiency of quasi-stationary reaction is specified by complete duration of all contacts on the encounter, and the time distribution, as is established, is exponential. Thus, the derived expression corresponds to the so-called kinematic

approximation in the theory of reactions proceeding in a narrow reaction zone. It is important that complete escape from the "cage complex" also means the escape from the cage to solution, since in the opposite case the time of being in contacts will vary due to re-contacts.

Despite exponential nature of distribution in complete residence time in contacts, the character of motion in the cage (giving rise to combination of re-contacts) increases substantially the residence time in the "cage complex" as compared to collision time in gases, and this affects the specific features of the reaction course in solution not typical of reaction in gases.

Most clearly, these peculiarities manifest themselves in the appearance of additional channels of reactant transformation in consecutive multistage reactions that cannot be caused by elementary event of chemical conversion. Rate constants of new transition channels depend essentially on the regime of intermediate and final stage of reaction. In the kinetic regime, the rate constants go to zero, and kinetic equations of formal chemical kinetics retain their traditional form corresponding to the given reaction mechanism (combination of elementary stages). For example, the rate constant of the initial stage of irreversible multistage reaction is redefined with allowance for diffusion in a traditional fashion, as in one-stage irreversible reaction. However, rate constants of additional transition channels become nonzero, if the above stages are affected by diffusion motion. Values of rate constants of additional transition channels increase and reach their maximum at diffusion control of intermediate and final stages. The appearance of such additional transition channels takes place in considering reversible reactions as well. However, unlike consecutive irreversible multistage reactions, the rate constant of the initial stage of multistage reaction is redefined with allowance for diffusion in a more complicated fashion than in one-stage reversible reaction.

These specific features of multistage consecutive reactions leading to the change in kinetic equations of formal chemical kinetics should be taken into consideration in finding rate constants on the basis of experimental kinetics analysis.

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