

Kinetic equations for exactly solvable models of a geminate reaction in the presence of scavengers

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Received 16 March 2005; accepted 22 June 2005

Available online 22 July 2005

Abstract

On the basis of two many-particle models of a geminate reaction $A + B \rightarrow \text{Product}$ in the presence of bulk scavengers C for which the closed kinetic equations for the mean concentration of species can be exactly derived the unified form of integro-differential equation of general kinetic theory is obtained. A clear physical interpretation has been done for every term of the equations. For low concentration $[C]$ of scavengers, the kinetic equations are reduced to the so-called quasi-binary ones that in turn are brought into the equivalent regular form (the rate type equations).

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Keywords: Kinetic equations; Many-particle approach; Binary theory; Elementary bulk reactions; Law of mass action; Scavengers problem

1. Introduction

A consistent many-particle approach to theoretical treatment of chemically reacting systems is the most powerful way of deriving of kinetic equations in liquid solutions. A many-particle derivation of kinetic equations of irreversible chemical reactions in rather dilute solutions in initially chemically homogeneous system was first performed by Waite [1,2] on the basis of the well-known method of superposition decoupling in the hierarchies for the Reduced Distribution Functions. Up today considerable progress has been achieved in the derivation of kinetic equations of bulk reversible elementary reactions [3–22] and multistage ones [23,24]. However, less attention has been given to the reacting systems with initial spatial correlations between the reacting particles. These correlations can be of two types. Correlations of the first type addressed to bulk

reactions are called the same-type correlations; they correspond to infinite correlation radii between reactants, and are taken into account in the consideration of simple irreversible reactions [25]. Initial correlations of the second type correspond to correlations with finite correlation radii that are inherent in reactions containing the so-called geminate stages. The simplest examples are the reactions of isolated geminate pairs [26]. More complicated cases are the reactions of non-isolated geminate pairs [27–31], isolated geminate pairs in dilute solution of scavengers [32–38], and, the most general case, non-isolated geminate pairs in solution of scavengers [39]. Many-particle consideration of irreversible reactions of these types has been performed in the literature on the basis of superposition decoupling [27,38,39]. However, it happened that using the superposition decoupling method in the derivation of kinetic equations of certain reaction types gave the results inconsistent both with simple physical considerations and with numerical simulation [9,10,17]. Thus superposition decoupling has been criticized in a number of papers [4,8,17]. So in testing

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approximate methods of solving the problem that are commonly used in the literature and searching for new methods for the derivation of kinetic equations in the framework of a many-particle approach, the exactly solvable models are of great interest. The explicit form of the kinetics for such models in the case of irreversible reaction of isolated geminate pairs in rather dilute solutions of scavengers has been recently found in the literature [40].

This case is of practical interest. It is often realized in radiation chemistry when radiation pulse results in an isolated (from other geminate pairs) geminate pair the partners of which take part in bulk reactions with particles from solution. For example, one has to deal with such reactions in studies of primary radiation chemical processes in liquid hydrocarbons doped with charge acceptor [41], in the investigation of irreversible trapping reaction of the hydrated electron and its equilibrated optically excited states and various “precursor states” by different oxidants [42], etc. In these cases, the scavengers react with partners of a single type thus accelerating their decay and decreasing geminate reaction yield. The problem of adequate description of such systems is known as a “scavenger problem” [35,37]. The following kinetic scheme describing the competition of geminate and bulk reactions has been considered: at the initial instant of time there exist a geminate pair AB which can irreversibly recombine



Here, P is a product of a geminate reaction. It may be a molecule originated as a result of bimolecular association or two molecules originated by the exchange reaction. The geminate pair is surrounded by bulk C particles able to react with one of geminate partners, namely, B detaching it from a geminate partner



It is assumed that C particles are in excess, so the concentration of C particles is not changed due to reaction (1.2).

The goal of this paper is to analyze the forms of kinetic equations that will be obtained on the basis of the explicit form of the kinetics for exactly solvable models of a multistage reaction given by Eqs. (1.1) and (1.2) [40].

The outline of the paper is as follows. In Section 2, we give the main assumptions and results for exactly solvable many-particle models of the reactions considered, namely, (i) the model of immobile B reactant and (ii) the model, where B reactant moves by stochastic jumps for long (in a microscopic scale) distances (the hopping model). Equations of the memory function type for the models are presented, and clear physical interpretation of every term of equations is done in Section 3. In Section 4, we define the so-called quasi-binary kinetics for

low concentration [C] of scavengers and show that the kinetics are involved in exact many-particle kinetics for both models under consideration. In Section 5, we reduce general kinetic equations to the quasi-binary ones. In Section 6, the derived quasi-binary equations are brought to the equivalent regular form (the rate type equations). The results are summarized in Conclusion.

2. Many-particle models

Consider the model of spatially uniform reacting system containing one geminate pair AB and scavengers C with bulk concentration [C]. Reaction (1.1) in the geminate pair AB gives the product P, and bulk reaction (1.2) with an excess of non-interacting (point) scavengers C detaching B reactant from a geminate pair to produce D reactant takes place. The force interaction between A and B particles can be included into consideration. These two elementary reactions will be referred to as P and D reaction channels, respectively.

At any moment t ($t > 0$) the system considered can be found in one of three states: in the state AB with the probability $P_{AB}(t)$, where the geminate pair exists, in the state AD with the probability $P_{AD}(t)$, where A and D reactants exist, and in the state P with the probability $P_P(t)$, where the product P exists. Then

$$P_{AB}(t) + P_{AD}(t) + P_P(t) = 1. \quad (2.1)$$

The system under consideration contains four species. The probabilities to find them in the reacting system are

$$\begin{aligned} \mathcal{P}_A(t) &= P_{AB}(t) + P_{AD}(t); & \mathcal{P}_B(t) &= P_{AB}(t); \\ \mathcal{P}_P(t) &= P_P(t); & \mathcal{P}_D(t) &= P_{AD}(t). \end{aligned} \quad (2.2)$$

By virtue of Eq. (2.1), we have

$$\mathcal{P}_A(t) + \mathcal{P}_P(t) = 1; \quad \mathcal{P}_B(t) + \mathcal{P}_D(t) + \mathcal{P}_P(t) = 1, \quad (2.3)$$

Note that due to normalization condition (2.3) the solution of the problem is expressed in terms of the probabilities $\mathcal{P}_B(t)$ and $\mathcal{P}_P(t)$. We shall call them the kinetics of B and P reactants, respectively.

The initial distribution of reactants in the geminate pair is specified by the distribution function $P(\vec{r}^A, \vec{r}^B) \equiv P(\vec{r}^A - \vec{r}^B)$ that is normalized

$$\int d\vec{r}^A P(\vec{r}^A - \vec{r}^B) = \int d\vec{r}^B P(\vec{r}^A - \vec{r}^B) = 1. \quad (2.4)$$

We assume that at the initial instant of time the distribution of C reactants is not correlated with the position of B.

Geminate reaction between A and B species and the bulk reaction between B and C species in the framework of exactly solvable models are defined by the reaction integral operators \hat{V}_{AB} and \hat{V}_{BC} with the following kernels [40]:

$$\begin{aligned}
V_{AB}(\vec{r}^A, \vec{r}^B, t | \vec{r}_0^A, \vec{r}_0^B, t_0) \\
= -w_{AB}(\vec{r}^A - \vec{r}^B) \delta(\vec{r}^A - \vec{r}_0^A) \delta(\vec{r}^B - \vec{r}_0^B) \delta(t - t_0), \\
V_{BC}(\vec{r}^B, \vec{r}^C, t | \vec{r}_0^B, \vec{r}_0^C, t_0) \\
= -w_{BC}(\vec{r}^B - \vec{r}^C) \delta(\vec{r}^B - \vec{r}_0^B) \delta(\vec{r}^C - \vec{r}_0^C) \delta(t - t_0).
\end{aligned} \quad (2.5)$$

Here $w_{AB}(\vec{r}^A - \vec{r}^B)$ and $w_{BC}(\vec{r}^B - \vec{r}^C)$ are usual elementary reaction rates, and $\delta(x)$ is delta-function. Thus the integral operators introduced act in a four-dimensional space of three spatial coordinates and time. Besides, we consider the entire time interval $-\infty < t < \infty$ introducing the Heaviside step function $\theta(t)$ for physical time interval $0 < t < \infty$. Such a space is often used in the literature on a many-particle problem [16–18] and is very convenient for further consideration. In the framework of this mathematical formalism, the functions $\theta(t)$ appear in rhs of Eqs. (2.1) and (2.3) instead of unities. Note that each of the reactants has internal coordinates, along with the mass center ones. However, in studies of many-particle aspects, taking account of internal coordinates leads to the complication of the theory, thus they are neglected in the present paper. In the general case, translational motion of A, B and C reactants in solution in the general case can be described by the Markovian process of random walks by stochastic jumps [40,43], and will be defined by the operators \hat{L}_A, \hat{L}_B and \hat{L}_C , respectively.

Even under the simplifying model assumptions made, it is rather difficult to find the kinetics of the reaction considered at all concentrations of C reactants. Therefore, we consider two particular models containing additional assumptions.

2.1. The model of immobile B particle

In this case, the kinetics $\mathcal{P}_B(t)$ of B reactant decay is as follows (in the thermodynamic limit) [40]:

$$\mathcal{P}_B(t) = P_{AB}^0 \Omega(t) N_B(t). \quad (2.6)$$

Here $P_{AB}^0 \equiv P_{AB}(t=0)$. Further we shall denote the initial conditions in a similar way. We introduce the survival probability $N_B(t)$ of immobile B particle in a bulk reaction the scavengers with the concentration $[C]$:

$$N_B(t) \equiv \theta(t) \exp \left\{ -[C] \int_0^t d\tau K(\tau) \right\}. \quad (2.7)$$

Here $K(t)$ is the time-dependent rate constant of the bulk reaction:

$$K(t) = - \int d\vec{r}^C \hat{V}_C \hat{G}_C | \delta(t) 1(\vec{r}^C) \rangle, \quad (2.8)$$

where the propagator \hat{G}_C describes the evolution of the bulk reaction pair B + C. Their kernel obeys the equation:

$$\begin{aligned}
(\partial_t - \hat{L}_C - \hat{V}_C) G_C(\vec{r}^C, t | \vec{r}_0^C, t_0 / \vec{r}^B) \\
= \delta(t - t_0) \delta(\vec{r}^C - \vec{r}_0^C),
\end{aligned} \quad (2.9)$$

where $V_{BC} = V_C \delta(\vec{r}^B - \vec{r}_0^B)$. Though the propagator \hat{G}_C depends parametrically on the coordinate of B reactant, reaction rate constant (2.8) of the bulk reaction does not depend on this coordinate. The survival probability of the geminate pair $\Omega(t)$ in Eq. (2.6) is defined in a common way [32,40]

$$\Omega(t) = \int d\vec{r}^A \hat{G}_A | \delta(t) P(\vec{r}^A - \vec{r}^B) \rangle, \quad (2.10)$$

where the propagator \hat{G}_A describes the evolution of the isolated geminate pair A + B. Its kernel satisfies the following equation:

$$\begin{aligned}
(\partial_t - \hat{L}_A - \hat{V}_A) G_A(\vec{r}^A, t | \vec{r}_0^A, t_0 / \vec{r}^B) \\
= \delta(t - t_0) \delta(\vec{r}^A - \vec{r}_0^A),
\end{aligned} \quad (2.11)$$

where $V_{AB} = V_A \delta(\vec{r}^B - \vec{r}_0^B)$. Note that the survival probability $\Omega(t)$ does not depend on the coordinate of B reactant.

The many-particle kinetics of the geminate reaction product $\mathcal{P}_P(t)$ is given by [40]

$$\mathcal{P}_P(t) = \theta(t) P_P^0 + P_{AB}^0 \int_0^t d\tau K_g(\tau) N_B(\tau). \quad (2.12)$$

Here, we introduce the geminate reaction rate $K_g(t)$ that is determined by an ordinary formula [40,44]:

$$K_g(t) = - \int d\vec{r}^A \hat{V}_A \hat{G}_A | \delta(t) P(\vec{r}^A - \vec{r}^B) \rangle. \quad (2.13)$$

As is easily seen, the relation:

$$\partial_t \Omega(t) = \delta(t) - K_g(t) \quad (2.14)$$

joins the survival probability of the geminate pair $\Omega(t)$ and the geminate reaction rate $K_g(t)$. The kinetics given by Eqs. (2.6) and (2.12) of exactly solvable model considered obeys the kinetic equations. The kinetic equation for the kinetics $\mathcal{P}_P(t)$ (and $\mathcal{P}_A(t)$ following from Eqs. (2.3) written in the mathematical space accepted) can readily be obtained by differentiating Eq. (2.12)

$$\begin{aligned}
\partial_t \mathcal{P}_P(t) &= \delta(t) P_P^0 + P_{AB}^0 K_g(t) N_B(t); \\
\partial_t \mathcal{P}_A(t) &= \delta(t) P_A^0 - P_{AB}^0 K_g(t) N_B(t).
\end{aligned} \quad (2.15)$$

The first term proportional to delta-function in the framework of the mathematical formalism used takes into account the initial condition. The second term gives the reaction rate in the channel P. It has a clear physical meaning: the rate of the product formation in a geminate pair surrounded by scavengers is the product of the reaction rate in an isolated pair and the survival probability of B reactant in a bulk reaction at time t . Statistical independence of both processes is a distinguishing feature of the particular model considered and, as it will be shown below, does not take place in the general case.

The kinetic equation for the kinetics $\mathcal{P}_B(t)$ can be obtained taking into account that the survival probability $N_B(t)$ obeys

$$\partial_t N_B(t) = \delta(t) - [C]K(t)N_B(t). \quad (2.16)$$

Then

$$\partial_t \mathcal{P}_B(t) = \delta(t)P_{AB}^0 - [C]K(t)\mathcal{P}_B(t) - P_{AB}^0 K_g(t)N_B(t). \quad (2.17)$$

At the first glance, the contributions of geminate P channel (the third term in Eq. (2.17)) and bulk D channel (the second term in Eq. (2.17)) to the rate of B reactant decay are additive and have a clear physical meaning. However, this fact is the feature of the particular model considered and does not take place in the general case. Besides, correct interpretation of contributions of reaction channels into the rate can be done only for equations written in the universal form of general kinetic theory.

2.2. The model with jumping B reactant (the hopping model)

In this model, the force interaction between B and C reactants is neglected, and the motion of B is taken into account. It is assumed that this motion is stochastic jumps of large length compared to reactants size. In the thermodynamic limit, this motion can be considered as jumps of infinite length. For example, the motion of such type approximates the motion of an electron in non-polar liquids quite well [45]. Thus the model with jumping B reactant differs essentially from that with immobile B, though both models coincide in a specific case where there is no force interaction between B and C, and B reactant is at rest ($\tau_B^{-1} = 0$). The last factor plays an important role providing continuity of results. For this model, the many-particle kinetics $\mathcal{P}_B(t)$ obeys the equation [40]

$$\mathcal{P}_B(t) = P_{AB}^0 \tilde{Q}(t) \tilde{N}_B(t) e^{-t/\tau_B} + \frac{1}{\tau_B} \int_{-0}^t d\tau \tilde{N}_B(t-\tau) e^{-(t-\tau)/\tau_B} \mathcal{P}_B(\tau). \quad (2.18)$$

Here and below the quantities referring to a specific case with B reactant at rest ($\tau_B^{-1} = 0$) in the model of jumping B reactant are marked by tilde. The many-particle kinetics $\mathcal{P}_P(t)$ is defined by the expression

$$\mathcal{P}_P(t) = P_P^0 \theta(t) + P_{AB}^0 \int_{-0}^t d\tau \tilde{K}_g(\tau) \tilde{N}_B(\tau) e^{-\tau/\tau_B}. \quad (2.19)$$

In a particular case $\tau_B^{-1} = 0$ it reduces to Eq. (2.12). As in Section 2.1, the kinetic equation for the kinetics $\mathcal{P}_P(t)$ is derived most easily. Differentiating Eq. (2.19), we have

$$\begin{aligned} \partial_t \mathcal{P}_P(t) &= \delta(t)P_P^0 + P_{AB}^0 \tilde{K}_g(t) \tilde{N}_B(t) e^{-t/\tau_B}; \\ \partial_t \mathcal{P}_A(t) &= \delta(t)P_A^0 - P_{AB}^0 \tilde{K}_g(t) \tilde{N}_B(t) e^{-t/\tau_B}. \end{aligned} \quad (2.20)$$

Comparison between Eqs. (2.20) and (2.15) shows that in the model at hand physical meaning of the reaction rate in P channel remains the same. Only the survival probability of B reactant in a geminate pair in the course of the bulk reaction is slightly modified. This probability is formed in the course of two parallel statistically independent processes: the decay of the pair due to the encounter of B with C, or because of the escape of B reactant by a jump of infinite length. Certainly, in the case of the jumps of finite length both processes will depend on one another.

3. Universal kinetic equations of general kinetic theory

It is known that calculation of a many-particle kinetics by the methods of a general kinetic theory yields inhomogeneous integro-differential kinetic equations [46–50]. For reactions (1.1) and (1.2), the kinetics $\mathcal{P}_B(t)$ obeys the equation

$$\begin{aligned} \partial_t \mathcal{P}_B(t) &= P_{AB}^0 \delta(t) - [C] \int_{-0}^t d\tau \Sigma(t-\tau) \mathcal{P}_B(\tau) \\ &\quad - [C] P_{AB}^0 I_D(t) - P_{AB}^0 I_P(t). \end{aligned} \quad (3.1)$$

It is a convolution type (retarded) equation that takes into account that the rate of bulk reaction (1.2) at the moment t is determined by concentration values at some previous moment τ . This type of equations expresses causal-consequence relation in the evolution of the reacting system in the most general manner. The kernel of this equation is commonly called the memory function. Inhomogeneous terms of the equation allow for initial spatial correlations of the reactants and are related to geminate reaction. The kinetic equation for the kinetics $\mathcal{P}_P(t)$ is of a similar, though more simple, structure

$$\partial_t \mathcal{P}_P(t) = \delta(t)P_P^0 + P_{AB}^0 I_P(t). \quad (3.2)$$

The kinetic equation for the accumulation kinetics $\mathcal{P}_D(t)$ of D product of reaction (1.2) with bulk scavengers C is immediately obtained from Eqs. (3.1), (3.2) and (2.3):

$$\begin{aligned} \partial_t \mathcal{P}_D(t) &= P_{AD}^0 \delta(t) + [C] \int_{-0}^t d\tau \Sigma(t-\tau) \mathcal{P}_B(\tau) \\ &\quad + [C] P_{AB}^0 I_D(t). \end{aligned} \quad (3.3)$$

The source $I_D(t)$ describes the influence of initial correlations on the kinetics $\mathcal{P}_D(t)$. Thus the structure of kinetic equations of the general kinetic theory allows us to extract the reaction channels of the multistage reaction considered in the explicit form.

We see that kinetic equations (2.15) and (2.20) for the kinetics $\mathcal{P}_P(t)$ have the structure of Eq. (3.2) of the general kinetic theory and include only one geminate channel of P product creation. Kinetic equation (3.3) includes D channel. Hence, the second and the third

terms in general Eq. (3.1) proportional to concentration $[C]$ of C reactants are determined by D channel of the reaction. We see that in the framework of the general kinetic theory ultimate contribution of this channel to the reaction rate of B reactant decay is divided between two subchannels. Physical interpretation of this fact follows.

We see that neither of equations (2.17) nor (2.18) governing the exact many-particle kinetics of the model at hand falls into the category of general kinetic theory equations. Thus it is necessary to show that kinetic equations (2.17) or (2.18) for both models considered can be transformed into the unified form of Eq. (3.1) of the general kinetic theory.

3.1. The model of immobile B particle

To obtain the kinetic equation in the form of general kinetic theory, Eq. (2.16) should be replaced by the equivalent integro-differential equation [12,17,51]

$$\partial_t N_B(t) = \delta(t) - [C] \int_{-0}^t d\tau \Sigma(t-\tau) N_B(\tau), \quad (3.4)$$

where the memory function $\Sigma(t)$ is defined by its Laplace transform

$$\Sigma^L(s) = \frac{(KN_B)^L(s)}{N_B^L(s)}. \quad (3.5)$$

Here and below the upper index L denotes the Laplace transforms of the corresponding quantities. This easily gives kinetic equation (3.1) where (see Eqs. (2.15))

$$I_P(t) = K_g(t) N_B(t). \quad (3.6)$$

The quantity $I_D(t)$ is defined by its Laplace transform

$$I_D^L(s) = (KN_B \Omega)^L(s) - (N_B \Omega)^L(s) \frac{(KN_B)^L(s)}{N_B^L(s)}. \quad (3.7)$$

Thus we see that the decay of B reactant really proceeds by two reaction channels: D and P, the last term in the rhs of Eq. (3.1) is the decay rate by geminate P channel. Hence, the second and the third terms proportional to the concentration of C reactants specify the decay rate by D channel. Thus D reaction channel is divided into two subchannels. We call them bulk D subchannel and geminate D subchannel, respectively. Physically, such a separation means the following. In the bulk D, subchannel B reactant escapes the geminate pair without any interaction (neither force nor reaction) with A reactant and decays on the encounter with bulk C reactants. In the geminate D subchannel, the decay of B reactant due to the encounter with C reactants occurs inside the geminate pair, i.e., is at least of essentially three-particle nature. To prove the validity of the above interpretation of the geminate D subchannel, it is necessary to reveal a microscopic essence of the quantity $I_D(t)$. For this purpose, in Eq. (3.7) we pass to originals using Eq. (3.5)

$$I_D(t) = \int_{-0}^t d\tau \Sigma(t-\tau) [\Omega(t) - \Omega(\tau)] N_B(\tau). \quad (3.8)$$

Now for the survival probability $\Omega(t)$ we use definition (2.10). For the propagator \hat{G}_A , we employ the representation

$$G_A(\vec{r}^A, t | \vec{r}_0^A, t_0) = \int d\vec{r}_1^A G_A(\vec{r}^A, t | \vec{r}_1^A, \tau) d\vec{r}_1^A G_A(\vec{r}_1^A, \tau | \vec{r}_0^A, t_0), \quad (3.9)$$

which is the relation of Chapman–Kolmogorov (Einstein–Smoluchowski) type [44]. We also introduce the propagator \hat{G}_A^{00} of A reactant free motion (in the absence of force and reaction interaction between A and B reactants) and take into account that the number of particles is preserved

$$\int d\vec{r}^A G_A^{00}(\vec{r}^A, t | \vec{r}_0^A, \tau) = \theta(t - \tau). \quad (3.10)$$

Thus Eq. (3.8) gives the desired representation for the quantity $I_D(t)$

$$I_D(t) = \int d\vec{r}^A [(G_A - \widehat{G_A^{00}}) \Sigma(t - t_0)] \times [N_B(t - t_0) G_A] | \delta(t) P(\vec{r}^A - \vec{r}^B) \rangle. \quad (3.11)$$

Here symbol $\widehat{[\dots]}$ denotes the operator with the kernel in square brackets. According to representation (3.11), the rate in the geminate D subchannel is formed as follows. By some instant of time t the survival probability of the geminate pair AB surrounded by “scavengers” is the evolution of the initial geminate correlation. Then B reactant decays on the encounter with C reactants, on condition that a geminate pair does not decompose (preservation of the geminate pair is determined by the propagator $(\hat{G}_A - \hat{G}_A^{00})$ describing the “scattered wave” [44]). So, generally speaking, in calculating the D subchannel term even for small concentrations $[C]$ (however, not in the case of the models considered), one has to do with a three-body problem.

3.2. The model with jumping B reactant (the hopping model)

The kinetic equations for B reactant are most conveniently derived using the Laplace transforms. The Laplace transform of the kinetics $\mathcal{P}_B(t)$ is easily found from Eq. (2.18) by a conventional procedure

$$\mathcal{P}_B^L(s) = \frac{P_{AB}^0 (\tilde{\Omega} \tilde{N}_B)^L(s + \tau_B^{-1})}{1 - \tau_B^{-1} \tilde{N}_B^L(s + \tau_B^{-1})}. \quad (3.12)$$

This equality identically gives the following:

$$s \mathcal{P}_B^L(s) = P_{AB}^0 - [C] \Sigma^L(s) \mathcal{P}_B^L(s) - [C] P_{AB}^0 I_D^L(s) - P_{AB}^0 I_P^L(s). \quad (3.13)$$

As is seen, the structure of Eq. (3.13) coincides with that of the Laplace transform of general kinetic equation (3.1). In Eq. (3.13), the Laplace transform of the memory function of the bulk D subchannel is [51]

$$\Sigma^L(s) = \frac{(\tilde{K}\tilde{N}_B)^L(s + \tau_B^{-1})}{\tilde{N}_B^L(s + \tau_B^{-1})} \quad (3.14)$$

and the Laplace transform $I_P^L(s)$ of $I_P(t)$ appearing as the source of geminate P channel in full accordance with Eq. (2.20) for the kinetics $\mathcal{P}(t)$, is

$$I_P^L(s) = (\tilde{K}_g\tilde{N}_B)^L(s + \tau_B^{-1}). \quad (3.15)$$

The Laplace transforms $I_D^L(s)$ of $I_D(t)$ appearing as the source of geminate D subchannel is

$$I_D^L(s) = (\tilde{K}\tilde{N}_B\tilde{\Omega})^L(z) - (\tilde{N}_B\tilde{\Omega})^L(z) \frac{(\tilde{K}\tilde{N}_B)^L(z)}{\tilde{N}_B^L(z)}, \quad (3.16)$$

where $z = s + \tau_B^{-1}$

Thus Eq. (3.13) is the Laplace transform of the desired kinetic equation. It has the form of kinetic equation (3.1), and physical meaning of its kinetic coefficients remains the same as in the previous case, despite the change of the model. Just slight modification of mathematical formulae in the definition of the coefficients takes place (compare Eqs. (3.14) and (3.5), as well as Eqs. (3.16) and (3.7)). As follows from Eqs. (3.13)–(3.16), in the general case the kinetic coefficients are expressed via the quantities of a particular case of immobile B in the model of jumping B reactant. This specific case is also a particular case of the model with immobile B reactant for which the kinetic coefficients have already been introduced by formulae (3.5) and (3.7) in Section 3.1. It is easily established that

$$\begin{aligned} \Sigma(t) &= e^{-t/\tau_B} \tilde{\Sigma}(t); & I_P(t) &= e^{-t/\tau_B} \tilde{I}_P(t); \\ I_D(t) &= e^{-t/\tau_B} \tilde{I}_D(t). \end{aligned} \quad (3.17)$$

The third equality from Eqs. (3.17) makes it possible to refine the microscopic meaning of $I_D(t)$ in the model under consideration. In view of Eq. (3.11), one has

$$\begin{aligned} I_D(t) &= \int d\vec{r}^A \left[(\tilde{G}_A - \tilde{G}_A^{00}) \widehat{\tilde{\Sigma}(t-t_0)} \exp \left\{ -\frac{t-t_0}{\tau_B} \right\} \right] \\ &\quad \times \left[\tilde{N}_B(t-t_0) \tilde{G}_A \exp \left\{ -\frac{t-t_0}{\tau_B} \right\} \right] |\delta(t) P(\vec{r}^A - \vec{r}^B)\rangle. \end{aligned} \quad (3.18)$$

Eq. (3.18) shows that, as in the case of P reaction channel, the hopping mobility of B reactant manifests itself in the rate of geminate D subchannel as an additional parallel statistically independent process of a geminate pair decay due to the jump of infinite length.

The relation between the kinetic coefficients of general and particular cases expressed in Eqs. (3.17) is rather useful. However, similar relation for geminate reaction rates should be added

$$K_g(t) = e^{-t/\tau_B} \tilde{K}_g(t). \quad (3.19)$$

This relation follows from Eq. (2.13) in view of

$$G_A(\vec{r}^A, t | \vec{r}_0^A, t_0 / \vec{r}^B) = \exp \left\{ -\frac{t-t_0}{\tau_B} \right\} \tilde{G}_A(\vec{r}^A, t | \vec{r}_0^A, t_0 / \vec{r}^B). \quad (3.20)$$

The propagator \hat{G}_A describes the evolution of an isolated geminate pair with allowance for the jump of infinite length of B reactant. Its kernel obeys the equation [40]

$$\begin{aligned} (\partial_t - \hat{L}_A - \hat{V}_A + \tau_B^{-1}) G_A(\vec{r}^A, t | \vec{r}_0^A, t_0 / \vec{r}^B) \\ = \delta(t-t_0) \delta(\vec{r}^A - \vec{r}_0^A). \end{aligned} \quad (3.21)$$

Note that the propagator \hat{G}_A from Eq. (3.20) cannot be used in Eq. (2.10), since even in the absence of the reaction between A and B partners of geminate pair ($\hat{V}_A = 0$) it does not preserve the number of A reactants. However, this demerit is insignificant, if \hat{G}_A is used in Eq. (2.13).

Thus on the basis of kinetic equations derived in this section for different models of the “scavenger” problem, we have introduced many-particle kinetic coefficients (memory functions and sources). In the range of low concentration of C reactants one can simplify them thus obtaining the desired low concentration kinetic equations. However, even for bulk reactions such simplifications present considerable difficulties [51]. The simplest and most effective test for the correctness of simplifications is the use of asymptotes at low densities of reactants of the many-particle kinetics, i.e., the so-called binary kinetics. Similar concepts for the “scavenger” problem will be given in the next section.

4. The quasi-binary kinetics

Binary kinetics is of primary importance in the derivation of kinetic equations of bulk reactions at low densities of reactants [51,52,54]. In this section, we introduce similar concepts for the “scavenger” problem. Further they will form the basis of the derivation of kinetic equations for low density of C reactants.

4.1. The model of immobile B particle

In the range of low concentrations [C] many-particle kinetics (2.6) and (2.12) can be simplified, if a binary estimate for the survival probability of B surrounded by C reactants is applied [12,17,51,52,54]

$$N_B(t) \simeq N^b(t) = \theta(t) e^{-[C]k_b t} \left(1 - [C] \int_{-0}^t d\tau \eta_b(\tau) \right). \quad (4.1)$$

The form of the binary kinetics $N^b(t)$ is universal (i.e., independent of models). In our model, k_b , the Markovian (stationary) part of the binary rate constant of the bulk reaction and $\eta_b(t)$, its non-Markovian part, are

$$k_b = \lim_{t \rightarrow \infty} K(t); \quad \eta_b(t) = K(t) - k_b \theta(t). \quad (4.2)$$

So the following low concentration asymptotes are easily obtained for many-particle kinetics $\mathcal{P}_B(t)$ and $\mathcal{P}_P(t)$:

$$\begin{aligned} \mathcal{P}_B(t) &\simeq \mathcal{P}_B^{\text{qb}}(t) \equiv P_{AB}^0 \Omega(t) N^b(t); \\ \mathcal{P}_P(t) &\simeq \mathcal{P}_P^{\text{qb}}(t) \equiv P_P^0 \theta(t) + P_{AB}^0 \int_{-0}^t d\tau K_g(\tau) N^b(\tau). \end{aligned} \quad (4.3)$$

Kinetics $\mathcal{P}_B^{\text{qb}}(t)$ and $\mathcal{P}_P^{\text{qb}}(t)$ appearing in Eqs. (4.3) will be called quasi-binary. This is because the bulk reaction is described in the frame of the binary approximation, i.e., the processes when a geminate pair is attacked by two or more C reactants from the volume are neglected. On the other hand, a geminate pair lifetime may turn out to be comparable to the decay time of the kinetics $N^b(t)$. This means that, generally speaking, the decay of B reactant in geminate and bulk reactions can be mutually dependent. Thus the necessity of considering a three-particle problem (geminate pair AB and C reactant) arises. The binary kinetics $N^b(t)$ allows for the first two terms of the asymptotic expansion in a binary scaling parameter of the many-particle kinetics [12,16]. The leading term of the expansion gives the Markovian kinetics

4.2. The model with jumping B reactant (the hopping model)

To obtain the quasi-binary approximation in this model, use the binary estimate

$$\begin{aligned} \tilde{N}_B(t) &\simeq \tilde{N}^b(t) \\ &= \theta(t) e^{-[C] \tilde{k}_b t} \left(1 - [C] \int_{-0}^t d\tau \tilde{\eta}_b(\tau) \right). \end{aligned} \quad (4.6)$$

The Markovian part \tilde{k}_b and non-Markovian part $\tilde{\eta}_b(t)$ of the binary rate constant are defined by analogy with Eq. (4.2), since they are a particular case of these definitions. As a result, Eq. (2.19) gives the following quasi-binary estimate for the many-particle kinetics $\mathcal{P}_B(t)$:

$$\begin{aligned} \mathcal{P}_B(t) &\simeq \mathcal{P}_B^{\text{qb}}(t) \\ &\equiv P_P^0 \theta(t) + P_{AB}^0 \int_{-0}^t d\tau \tilde{K}_g(\tau) \tilde{N}^b(\tau) e^{-\tau/\tau_B}. \end{aligned} \quad (4.7)$$

Equation (3.19) easily shows that the dependence of the second term in the rhs of Eq. (4.7) on the parameters of spatial mobility of reactants does not reduce solely to that of relative migration parameters of reactants of the reaction pairs, as in Eqs. (4.3). In other words, in the model under consideration the quasi-binary kinetics exhibits its three-particle nature explicitly. The reasons have been given above. It is convenient to obtain the quasi-binary approximation for the kinetics $\mathcal{P}_P(t)$ using the Laplace transforms. With Eq. (4.6) in Eq. (4.7), we have

$$\mathcal{P}_B^L(s) \simeq P_{AB}^0 \frac{1 - \tilde{K}_g^L(z) - [C] \tilde{\eta}_b^L(z) + [C] z \left(\int_{-0}^t d\tau_1 \tilde{K}_g(\tau_1) \int_{-0}^t d\tau_2 \tilde{\eta}_b(\tau_2) \right)^L(z)}{s + [C] \tilde{K}_b + \tau_B^{-1} [C] \tilde{\eta}_b^L(z)}, \quad (4.8)$$

which corresponds to the kinetic law of mass action of formal chemical kinetics [53].

$$N^b(t) \simeq N^m(t) \equiv \theta(t) \exp(-[C] k_b t). \quad (4.4)$$

By analogy, further we shall separate out quasi-Markovian parts in quasi-binary kinetics of the “scavenger” problem

$$\begin{aligned} \mathcal{P}_B^{\text{qb}}(t) &\simeq \mathcal{P}_B^{\text{qm}}(t) \equiv P_{AB}^0 \Omega(t) N^m(t); \\ \mathcal{P}_P^{\text{qb}}(t) &\simeq \mathcal{P}_P^{\text{qm}}(t) \equiv P_P^0 \theta(t) + P_{AB}^0 \int_{-0}^t d\tau K_g(\tau) N^m(\tau). \end{aligned} \quad (4.5)$$

Thus in the quasi-Markovian approximation the bulk reaction is described in the frame-work of the kinetic law of mass action. Similar expressions (a sort of the mean-field approximation) have been used in the literature devoted to the “scavenger” problem [34–38,41].

where $z = s + \tau_B^{-1} + [C] \tilde{K}_b$. However, Eq. (4.8) is not a final result, since even in a particular case of the bulk reaction ($\tilde{K}_g = 0$) it involves the overestimation of accuracy [51]. To determine the orders to be kept within the limits of the binary conception, one should single out a zero in the denominator of Eq. (4.8) using the relation between the binary rate constants of the bulk reaction: $K_b(t) = k_b + \eta_b(t)$ for the general case and $\tilde{K}(t)$ for particular case $\tau_b^{-1} = 0$, respectively. Considering Markovian k_b or \tilde{k}_b and non-Markovian $\eta_b(t)$ or $\tilde{\eta}_b$ (see Eq. (4.2)) parts of the constants, we have [51]

$$\begin{aligned} k_b &= \tilde{k}_b + \tau_B^{-1} \tilde{\eta}_b^L(\tau_B^{-1}); \\ s \eta_B^L(s) &= (s + \tau_B^{-1}) \tilde{\eta}_b^L(s + \tau_B^{-1}) - \tau_B^{-1} \tilde{\eta}_b^L(\tau_B^{-1}). \end{aligned} \quad (4.9)$$

Then it is necessary to expand the remaining regular part of expression (4.8) in concentration [C] powers in the vicinity of the zero. In this case, an ambiguity arises related to the fact that in the binary approximation

$$\tilde{\eta}^L(s + \tau_B^{-1} + [C]k_b) \simeq \tilde{\eta}^L(s + \tau_B^{-1} + [C]\tilde{k}_b). \quad (4.10)$$

The above ambiguity is removed by the requirement for the fulfillment of the following property: in the case of ultrafast geminate reaction

$$\tilde{K}_g(t) = \tilde{\omega}_\infty \delta(t) \quad (4.11)$$

the kinetics $\mathcal{P}_B(t)$ at all $t > 0$ should coincide with the binary kinetics of the bulk reaction for which the initial conditions are re-defined, i.e., the following estimate should be valid:

$$\mathcal{P}_B(t) \simeq P_{AB}^0 \Omega_\infty N^b(t); \quad \Omega_\infty = 1 - \tilde{\omega}_\infty. \quad (4.12)$$

The quantity Ω_∞ is the survival probability of reactants of an isolated geminate pair by the moment of their infinite removal from one another. As a result, Eq. (4.8) gives the expression for the Laplace transform of the quasi-binary kinetics

$$\mathcal{P}_B^L(s) \simeq (\mathcal{P}_B^{qb})^L(s) \equiv \mathcal{P}_{AB}^0 \frac{1 - \tilde{K}_g^L(z) + [C]A^L(s)}{s + [C]k_b}. \quad (4.13)$$

Here the function $A(t)$ defines the non-Markovian part of the quasi-binary kinetics. It is defined by its Laplace transform

$$A^L(s) = z \left(\int_{-0}^t d\tau_1 \tilde{K}_g(\tau_1) \int_{-0}^t d\tau_2 \tilde{\eta}_b(\tau_2) \right)^L (z) - \eta_b^L(s + [C]k_b) + \tilde{K}_g^L(z) [\eta_b^L(s + [C]k_b) - \tilde{\eta}_b^L(z)], \quad (4.14)$$

where $z = s + \tau_B^{-1} + [C]\tilde{k}_b$. In the quasi-Markovian approximation $A(t) = 0$, thus, after recovering the original (in view of Eq. (3.18)), Eq. (4.13) yields the expression for the quasi-Markovian kinetics in the model with jumping B reactant

$$\begin{aligned} \mathcal{P}_B(t) &\simeq \mathcal{P}_B^{qm}(t) \equiv P_{AB}^0 \int_{-0}^t d\tau e^{-[C]k_b(t-\tau)} [\delta(\tau) - K_g(\tau) e^{-[C]\tilde{k}_b\tau}] \\ &\equiv P_{AB}^0 e^{-[C]k_b t} \int_0^t d\tau e^{-[C](\tilde{k}_b - k_b)\tau} \partial_\tau \Omega(\tau). \end{aligned} \quad (4.15)$$

This expression does not coincide with the expression obtained in the framework of the “mean-field” approximation [34–38,41]. Only at $k_b = \tilde{k}_b$ the quasi-Markovian kinetics is factorized and coincides with the first expression from Eqs. (4.5). Note that, according to Eqs. (4.15), the quasi-Markovian kinetics (just as the quasi-binary one) is of three-particle nature and cannot be expressed in terms of the relative mobility of reactants in pairs AB and BC.

5. The quasi-binary kinetic equations

Derivation of quasi-binary equations is based on the reduction of many-particle kinetic equations (3.1) and

(3.2) to low concentration limit of C reactants. Obviously, the structure of basic kinetic equations remains unchanged

$$\begin{aligned} \partial_t \mathcal{P}_B^{qb}(t) &= P_{AB}^0 \delta(t) - [C] \int_{-0}^t d\tau \Sigma^b(t-\tau) \mathcal{P}_B^{qb}(\tau) \\ &\quad - [C] P_{AB}^0 I_D^{qb}(t) - P_{AB}^0 I_P^{qb}(t) \end{aligned} \quad (5.1)$$

and

$$\partial_t \mathcal{P}_P^{qb}(t) = \delta(t) P_P^0 + P_{AB}^0 I_P^{qb}(t), \quad (5.2)$$

where the upper indices mean the quasi-binary approximation. Now the problem is to correctly simplify the quantities $\Sigma(t)$, $I_P(t)$, and $I_D(t)$ in Eqs. (3.1) and (3.2) so as to derive quantities $\Sigma^{qb}(t)$, $I_P^{qb}(t)$ and $I_D^{qb}(t)$.

5.1. The model of immobile B particle

Most easily, this can be done for Eq. (3.6) using estimate (4.1). So, we have the following quasi-binary quantity:

$$I_P^{qb}(t) = K_g(t) N^b(t). \quad (5.3)$$

It is readily seen that the quasi-binary kinetics $\mathcal{P}_P^{qb}(t)$ from Eqs. (4.3) is the exact solution of Eq. (5.2).

A binary estimate for the memory function $\Sigma(t)$ is based on its representation as a sum of Markovian and non-Markovian parts [51]

$$\Sigma(t) = \Sigma_m(t) + \Sigma_n(t). \quad (5.4)$$

Generally speaking, in the expansion in concentration $[C]$ powers each of the terms involves all powers. In the binary approximation it will suffice to consider the main orders in each of them. However, for the non-Markovian part it is necessary to preserve its principle property [51]

$$\Sigma_n^L(s) = -[C]K_m = 0, \quad (5.5)$$

where K_m is a many-particle Markovian rate constant the existence of which for the models in question has been proved in [51]. So the expansion of the non-Markovian part is made after the extraction of the Markovian exponent. As a result, in the binary approximation we have the following estimates [12,17,51]:

$$\begin{aligned} \Sigma^b(t) &= \Sigma_m^b(t) + \Sigma_n^b(t); \quad \Sigma_m^b(t) \simeq k_b \delta(t); \\ \Sigma_n^b(t) &= e^{-[C]k_b t} \partial_t \eta_b(t). \end{aligned} \quad (5.6)$$

Such a complicated dependence on concentration $[C]$ of the non-Markovian part is related to the fact that actually the expansion was performed in the binary scaling parameter rather than in $[C]$ powers [12,16]. To expand a many-particle source (3.8) in the binary scaling parameter, it is necessary to establish its exact property (the analog of Eq. (5.5)) which could allow one to get rid of the terms falling beyond the limits of the quasi-binary approximation in the range of small $[C]$ concentrations.

This property manifests itself in the consideration of ultrafast geminate reaction (see Eq. (4.11)). In fact, it was employed in the derivation of the quasi-binary kinetics in Section 4. As is easily seen from Eqs. (3.8) and (3.17), in both models under discussion we have for ultrafast geminate reaction

$$I_D(t) = 0; \quad \text{if } K_g(t) = \omega_\infty \delta(t). \quad (5.7)$$

In other words, the geminate D subchannel disappears, since the lifetime of the geminate pair is too short for a scavenger from the volume to approach it. Obviously, this property is of a general character and is not associated with specific properties of the models. In the range of small $[C]$ concentrations source (3.8) can be simplified using estimates (4.1) and (5.6). So we get the estimate satisfying Eq. (5.7)

$$I_D(t) \simeq I_D^{\text{qb}}(t) \equiv e^{-[C]k_b t} \int_{-0}^t d\tau K_g(\tau) [\eta_b(t-\tau) - \eta_b(t)]. \quad (5.8)$$

In full agreement with physical interpretation, $I_D^{\text{qb}}(t) \leq 0$, since the integrand in Eq. (5.8) is non-negative because the function $\eta_b(t)$ is a monotonically decreasing function. Note that the non-Markovian term in the first Eq. (5.6) is of the next order of smallness in the scaling parameter as compared to the Markovian one [12,16], so it can be taken into account by the perturbation theory methods. This will be used below. In particular, it can readily be verified that the solution of Eq. (5.1) is approximated by the quasi-binary kinetics $\mathcal{P}_B^{\text{qb}}(t)$ from Eqs. (4.3). This proves the correctness of estimate (5.8).

5.2. The model with jumping B reactant

As before, the quasi-binary estimate of $I_P(t)$ is most easy to derive. Using estimate (4.6) in a many-particle kinetic equation (2.20), we have

$$I_P^{\text{qb}}(t) = \tilde{K}_g(t) \tilde{N}^b(t) e^{-t/\tau_B}. \quad (5.9)$$

At $\tau_B^{-1} = 0$ the above equation reduces to Eq. (5.3). Quasi-binary kinetics (4.7) is the exact solution of Eq. (5.2). To obtain a quasi-binary value of the memory function $\Sigma(t)$, turn to Eq. (3.14). We have [51]

$$\Sigma^L(s) \simeq (\Sigma^b(t))^L \\ = k_b + (s + [C]k_b)\eta_b^L(s + [C]k_b). \quad (5.10)$$

Recovering the original for the binary memory function yields representation (5.6), i.e., the binary memory function representation in terms of binary rate constant is of invariant form (depends on the relative mobility only), just as it should be, since it specifies the rate in bulk D subchannel. The quasi-binary estimate of the geminate D subchannel source $I_D(t)$ is based on Eq. (5.8) and the third equation from Eqs. (3.17). Thus

$$I_D^{\text{qb}}(t) = e^{-([C]k_b + \tau_B^{-1})t} \int_{-0}^t d\tau \tilde{K}_g(\tau) [\tilde{\eta}_b(t-\tau) - \tilde{\eta}_b(t)]. \quad (5.11)$$

Obviously, for the quasi-binary source $I_D^{\text{qb}}(t)$ property (5.7) holds. Eq. (3.1) easily gives the Laplace transform of the quasi-binary kinetic equation for the model at hand

$$s\mathcal{P}_B^L(s) = P_{AB}^0 - [C](\Sigma^b)^L(s)\mathcal{P}_B^L(s) - [C]P_{AB}^0(I^{\text{qb}})^L(s) \\ - P_{AB}^0(\tilde{K}_g\tilde{N}^b)^L(s + \tau_B^{-1}). \quad (5.12)$$

It can be shown that quasi-binary kinetics (4.13) is an approximate solution of Eq. (5.12) (up to the first order of the perturbation theory).

6. Regular form of quasi-binary kinetic equations

In the absence of geminate reaction ($K_g = 0$) kinetic equation (5.1) reduces to a kinetic equation of the Modified Encounter Theory (MET) [52,54]. So, just as MET, it should be brought into the so-called regular form satisfying the main principles of the kinetic theory. To transform this equation, we introduce the propagator \hat{H}_{mf} of Eq. (5.1), i.e., the memory function propagator

$$\partial_t H_{\text{mf}}(t|t_0) = \delta(t - t_0) - [C] \int_{-0}^t d\tau \Sigma^b(t-\tau) H_{\text{mf}}(\tau|t_0). \quad (6.1)$$

The kernel $H_{\text{mf}}(t|t_0)$ describes the non-Markovian bulk evolution of B reactant found itself in the volume at the instant of time t_0 . The evolution is induced by binary encounters of B reactant with C reactants. The efficiency of the encounters is defined by the memory function $\Sigma^b(t)$ (5.6). The explicit form of the propagator \hat{H}_{mf} kernel can be found from Eq. (6.1) by the perturbation method. As a result, the explicit form of the kernel $\Sigma^b(t)$ is taken into accounts

$$H_{\text{mf}}(t|t_0) = \theta(t - t_0) e^{-[C]k_b(t-t_0)} \left[1 - [C] \int_{-0}^{t-t_0} d\tau \eta_b(\tau) \right]. \quad (6.2)$$

The second term in square brackets in Eq. (6.2) is a small non-Markovian correction to the first term. In the binary approximation, this correction describes the establishment of a stationary profile in the neighborhood of C reactant in the course of a bulk reaction [51,55]. Of course, the start of the process coincides with the moment of B reactant escape from the cage, i.e., with the instant of time t_0 .

From the standpoint of the kinetic theory, an essential demerit of Eq. (6.1) is that in the frame of binary conception there exists the dependence of the memory function $\Sigma^b(t)$ (5.6) (as a kinetic coefficient) on the values of the initial concentration of reactants (in particular, on

concentration $[C]$). Thus the propagator defining the binary bulk evolution should be brought into a different form. For this purpose, consider the propagator \hat{H}_{re} of Eq. (2.17) which has the form of a rate equation. Its kernel is defined by the equation

$$\partial_t H_{\text{re}}(t|t_0) = \delta(t - t_0) - [C]K_b(t)H_{\text{re}}(t|t_0) \quad (6.3)$$

the kinetic coefficient of which is free of the above demerit. Just as the propagator $\hat{H}_{\text{mf}}, \hat{H}_{\text{re}}$ describes the non-Markovian bulk evolution of B reactant found itself in the volume at the instant of time t_0 . However, it is assumed that the process of the stationary profile establishment in the neighborhood of C reactant started at the moment $t = 0$. It is seen from the explicit form of the propagator kernel

$$H_{\text{re}}(t|t_0) = \theta(t - t_0)e^{-[C]k_b(t-t_0)} \left[1 - [C] \int_{t_0}^t d\tau \eta_b(\tau) \right] \quad (6.4)$$

following from solution of Eq. (6.3) by the perturbation method. Thus there is no correlation between B reactant escape from the cage and the start of the stationary profile formation in the neighborhood of C reactant in the non-Markovian bulk evolution described by the propagator \hat{H}_{re} . In the absence of geminate reaction ($K_g = 0$) the moment of B reactant escape from the cage coincides with the initial instant of time ($t_0 = 0$). Thus Eqs. (6.2), (6.4) and (4.1) yield

$$H_{\text{mf}}(t|0) = H_{\text{re}}(t|0) = N^b(t). \quad (6.5)$$

In the binary approximation, this is the basis for the transformation of the integro-differential kinetic equation into the differential one in the case of a bulk irreversible reaction [17,20,51]. However, for the “scavenger” problem $t_0 \neq 0$, and the distinctions between propagators \hat{H}_{mf} and \hat{H}_{re} become essential. Nevertheless, the propagator \hat{H}_{re} forms the basis for the construction of a regular form of the propagator \hat{H}_{mf} . Comparison between Eqs. (6.2) and (6.4) in the framework of the binary approximation gives the desired representation for the propagator \hat{H}_{mf}

$$\hat{H}_{\text{mf}} = \hat{H}_{\text{re}} - \hat{H}_{\text{syn}}. \quad (6.6)$$

Here we introduce the synchronization propagator \hat{H}_{syn} defined by the kernel

$$H_{\text{syn}}(t|t_0) = [C]\theta(t - t_0)e^{-[C]k_b(t-t_0)} \int_{t_0}^t d\tau [\eta_b(\tau - t_0) - \eta_b(\tau)] \quad (6.7)$$

that obeys the equation

$$\begin{aligned} \partial_t H_{\text{syn}}(t|t_0) = & -[C]k_b H_{\text{syn}}(t|t_0) + [C]\theta(t - t_0)e^{-[C]k_b(t-t_0)} \\ & \times [\eta_b(t - t_0) - \eta_b(t)]. \end{aligned} \quad (6.8)$$

In quasi-binary non-Markovian evolution this propagator is responsible for making allowance for time correla-

tions determined by the cause-consequence relation between B reactant escape from the cage and the start of the stationary profile formation in the neighborhood of C reactant. As is seen from Eq. (6.7), in the Markovian approximation $\hat{H}_{\text{syn}} = 0$. Hence, taking account of time correlations is needed solely in the non-Markovian approach, when a finite duration of the binary encounters of reactants is taken into consideration. Note that H_{syn} is a positive function (since the non-Markovian part $\eta_b(t)$ of the rate constant is a monotonically decreasing function). Thus making allowance for synchronization effects accelerates the course of bulk irreversible reaction in the “scavenger” problem. So the search for a regular form of kinetic quasi-binary equation (5.1) gives rise to the necessity of introducing a new notion of the binary theory, namely, synchronization propagator. Obviously, the reasons have nothing to do with specific features of a many-particle model of the “scavenger” problem discussed in this section. Such a necessity is determined by integro-differential form of inhomogeneous quasi-binary kinetic equation (5.1).

It is interesting to explicitly extract the contribution made by synchronization effects from quasi-binary kinetics. Conventional Green functions procedure makes it possible to find the solution of quasi-binary equation (5.1) by the perturbation method

$$\mathcal{P}_B(t) \simeq P_{\text{AB}}^0 [N^b(t) - \hat{H}_{\text{mf}}[C]I_D^{\text{qb}}(t) + I_P^{\text{qb}}(t)]. \quad (6.9)$$

Using Eq. (6.6) and retaining the terms up to the first two orders of the perturbation theory by the value of the non-Markovian part of the rate constant, we get the desired representation for the quasi-binary kinetics

$$\mathcal{P}_B(t) \simeq P_{\text{AB}}^0 [N^b(t) - \hat{H}_{\text{re}}[C]I_D^{\text{qb}}(t) + I_P^{\text{qb}}(t) + \hat{H}_{\text{syn}}|I_P^{\text{qm}}(t)], \quad (6.10)$$

where $I_P^{\text{qm}}(t)$ is the quasi-Markovian approximation of the source I_P^{qb} (see Eqs. (5.3) or (5.9) where $N^b(t)$ or $\tilde{N}^b(t)$ are defined by Eq. (4.4) or similar expression). The last term in square brackets describes the synchronization effect contribution to the quasi-binary kinetics. As it is positive, on the whole, making allowance for of synchronization retards the decay of B reactants. This agrees with a general rule that taking any correlation into consideration leads to retardation of the irreversible reaction kinetics decay.

To obtain the equation governing kinetics (6.10), we operate on Eq. (6.10) by $\partial_t + [C]K_b(t)$ and in view of Eq. (6.8). This gives the desired regular form for quasi-binary equation (5.1)

$$\begin{aligned} \partial_t \mathcal{P}_B(t) = & P_{\text{AB}}^0 \delta(t) - [C]K_b(t)\mathcal{P}_B(t) \\ & + [C]P_{\text{AB}}^0 [I_{\text{syn}}(t) - I_D^{\text{qb}}(t)] - P_{\text{AB}}^0 I_P^{\text{qb}}(t), \end{aligned} \quad (6.11)$$

where

$$[C]I_{\text{syn}}(t) = \hat{H}_{\text{syn}}|I_P^{\text{qm}}(t). \quad (6.12)$$

Comparison between Eqs. (5.1) and (6.11) shows that in a regular form the description of the rate in the bulk D sub-channel of the reaction is given by two terms (the second and the third ones in the rhs of Eq. (6.11)): homogeneous and inhomogeneous terms. Contribution to the Markovian reaction rate is made by the homogeneous term only. Its non-Markovian part describes the effects determined by correlations arising in the course of the bulk irreversible reaction (formation of a stationary profile in the neighborhood of C reactant). According to the foregoing, the inhomogeneous term allows for synchronization effects resulting from a finite life time of a geminate pair. Thus transition to a regular form of quasi-binary equation has made it possible to separate two types of correlations defining the non-Markovian rate in the bulk subchannel of D channel of the reaction of the “scavenger” problem. Note that the inhomogeneous term cannot be treated as an additional transition channel, because this term is positive. Further the inhomogeneous term will be called a synchronization source. We shall calculate $I_{\text{syn}}(t)$ for both models under consideration.

6.1. The model of immobile B particle

Taking into account that for this model

$$I_{\text{P}}^{\text{qm}}(t) = \theta(t) K_{\text{g}}(t) \exp(-[C] k_{\text{b}} t) \quad (6.13)$$

we obtain

$$I_{\text{syn}}(t) = e^{-[C] k_{\text{b}} t} \int_{-0}^t d\tau K_{\text{g}}(\tau) [\eta_{\text{b}}(t - \tau) - \eta_{\text{b}}(t)]. \quad (6.14)$$

Comparison of Eqs. (6.14) and (5.8) shows that for this model $I_{\text{syn}}(t) = I_{\text{D}}^{\text{qb}}(t)$. Then kinetic equation (6.11) is reduced to

$$\partial_t \mathcal{P}_{\text{B}}(t) = P_{\text{AB}}^0 \delta(t) - [C] K_{\text{b}}(t) \mathcal{P}_{\text{B}}(t) - P_{\text{AB}}^0 I_{\text{P}}^{\text{qb}}(t). \quad (6.15)$$

Such a radical simplification of quasi-binary equation (6.11) is accidental, peculiar solely to the specific model of the “scavenger” problem under discussion. It disappears even when the hopping mobility of B reactant is taken into account (i.e., in the case of the second model).

6.2. The model with jumping B reactant (the hopping model)

Since for this model,

$$\begin{aligned} I_{\text{P}}^{\text{qm}}(t) &= \theta(t) \tilde{K}_{\text{g}}(t) \exp(-(1/\tau_{\text{B}} + [C] \tilde{k}_{\text{b}} t)) \\ &\equiv \theta(t) K_{\text{g}}(t) \exp(-[C] \tilde{k}_{\text{b}} t) \end{aligned} \quad (6.16)$$

we have

$$I_{\text{syn}}(t) = e^{-[C] \tilde{k}_{\text{b}} t} \int_{-0}^t d\tau K_{\text{g}}(\tau) e^{-[C] (\tilde{k}_{\text{b}} - k_{\text{b}}) \tau} [\eta_{\text{b}}(t - \tau) - \eta_{\text{b}}(t)]. \quad (6.17)$$

Comparison between Eqs. (6.17) and (5.11) shows that now $I_{\text{syn}}(t) \neq I_{\text{D}}^{\text{qb}}(t)$. Then quasi-binary equation (6.11)

is the equation of the final form and cannot be simplified. Thus one can see that this kinetic equation does not coincide with the equation derived in the framework of superposition decoupling [39]. It contains extra inhomogeneous term (source) from D reaction channel, that is of essentially three-particle nature. Besides, the inhomogeneous term (source) from geminate P channel is of three particle nature too.

7. Conclusion

Using explicit expressions for two many-particle exactly solvable models of the “scavenger problem”, we have derived universal kinetic equations (3.2) and (3.3) of general kinetic theory for accumulation kinetics of geminate reaction (1.1) product P, and bulk reaction (1.2) product D with bulk scavengers C in excess. We see that in the framework of general kinetic theory the ultimate contribution of the latter channel to the decay rate of B reactant or to the accumulation rate of D species is divided between two subchannels. In the bulk D subchannel B reactant escapes from a geminate pair without any interaction (neither force nor reaction) with A reactant and decays on the encounter with bulk C reactants. This reaction is described by the memory function $\Sigma(t)$ that expresses causal-consequence relation in the bulk evolution of the reacting system. In geminate D subchannel the decay of B reactant due to the encounter with C reactants occurs inside a geminate pair, i.e., is at least of essentially three-particle nature and is described by the source term in kinetic equations.

At rather low concentrations $[C]$ of scavengers bulk D subchannel includes binary encounters only, and the memory function $\Sigma_{\text{b}}(t)$ depends on the relative motion of B and C reactants. However, geminate D subchannel and geminate P channel preserve their many-particle (three-particle) nature and, in general, cannot be expressed solely in terms of the relative mobility of reactants in reacting pairs BC and AB as it should be in pure binary theories. For this reason, the equations are called quasi-binary ones. Quasi-binary equations derived have been reduced to the so-called regular form of the commonly used rate equations with bulk reaction rate constant independent of concentration $[C]$ and inhomogeneous terms (sources) that take into account initial spatial correlations of reactants. However, these equations differ essentially from those available in the literature [39], since they involve additional source (connected with geminate D subchannel) and the sources are of essentially three-particle nature.

Thus the analysis of the forms of kinetic equations performed is very important for consistent many-particle derivation of correct kinetic equations for “scavenger” and related problems. A consistent systematic many-particle derivation of kinetic equations for the

“scavenger problem” at small concentration C of scavengers will be done elsewhere.

Acknowledgments

The authors are grateful to the Russian Foundation of Basic Research (RFBR) for financial support under the project 02-03-32182.

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