

Accumulation and Decay of Macroscopic Correlations in Elementary Reactions Kinetics[†]

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In the present contribution the Encounter Theory (ET) (the prototype of the classical Collision Theory in rarefied gases) concepts for widely occurring diffusion assisted irreversible bulk reactions $A + A \rightarrow C$ and $A + B \rightarrow C$ in liquid solutions examined by the authors in the literature are analyzed and compared with each other for these different types of reactions. It is shown that for a particular case of equal initial concentrations $[A]_0 = [B]_0$ in the reaction $A + B \rightarrow C$, when the kinetics of both reactions $A + A \rightarrow C$ and $A + B \rightarrow C$ in the framework of formal chemical kinetics and ET are the same, the accumulation of macroscopic correlations breaking the concepts of independent encounters and leading to the Generalized Encounter Theory (GET) are drastically different. The influence of the force interaction and the decay of nonstable reactants on the time behavior the macroscopic correlations is also briefly discussed.

Key Words : Elementary reaction, Kinetics, Correlations, Smoluchowski, Encounter theory

Introduction

Development of the theory of diffusion controlled reactions is related to the Smoluchowski works on coagulation theory in colloid chemistry.¹ Extension of these works to the theory of chemical reactions in liquid solutions has led to the so-called Smoluchowski approach and its subsequent generalizations to the general case of reacting contact sphere² or remote reactions.³⁻⁸ In the frame of this approach the kinetic equations have the form of differential ones (rate equations) similar to formal chemical kinetics equations with the only difference that the reaction rate constant is time dependent. Later on, traditional approaches to the derivation of kinetic equations in the theories of reactions in solutions based on the concepts of independent reactant pairs ("free pairs"^{9,10}) confirmed the results of the Smoluchowski approach. The exact many-particle (with respect to reactants) substantiation of these theories was performed for the simplest irreversible reaction using the so-called "target model",^{7,8} and at small concentrations - by Waite using superposition decoupling in hierarchies for Reduced Distribution Functions.⁹⁻¹¹ Low concentration of reactants means that the inequality takes place

$$\xi \equiv 4\pi R_{eff}^3 \cdot \max\{[A]_t, [B]_t\} \ll 1, \quad (1.1)$$

where R_{eff} is the effective radius of the reaction (for example, the rate constant for diffusion assisted reactions is defined by the relation $k = 4\pi R_{eff} D$, where D is the relative diffusion coefficient), while $[A]_t$ and $[B]_t$ are concentrations of the corresponding reactants. Note that the smallness of concentration of reactants in the development of a general theory of

reactions is also necessary because at high concentrations the reactants move in solution the composition of which is affected by the reaction.

However, these approaches turned out to be inapplicable in the investigation of dynamic physicochemical processes (determined by the Hamiltonians) and reversible chemical reactions.

So to consider these processes in liquid solutions, the approach has been proposed based on the fact that in the case of a traditional treatment of a solvent as a continual medium dilute solutions resemble a "gas" of reactants dissolved in a homogeneous chemically inert medium. So the development of the kinetic theory of physicochemical processes in solutions under condition (1.1) may be based^{12,13} on the analogy with the classical Collision Theory (CT) in gases,^{14,15} when the reacting particles are for the most part in the process of free walks in the bulk, and the reaction occurs upon their collisions the characteristic duration of which is essentially less than the mean time between them.

However, unlike gases, the solvent, though chemically inert, has a significant effect on the reaction course. On the one hand, it often causes fast relaxation in a quantum system of the interacting reactants, thus simplifying essentially the quantum dynamics (including rotational one) of the event of chemical conversion.¹⁶ In particular it results in the formation of the elementary event rate (sink term). The coordinate q of the configuration space in the general case includes space coordinates of all reactants, their orientation angles and other internal degrees of freedom (for example, vibrations, spin states, etc.). Calculation of the rate $w(q)$ (sink term) is a separate problem of the elementary event theory.¹⁷⁻¹⁹ In the kinetic theory of reactions depending on reactant mobility the rate $w(q)$ is considered to be given. Thus traditional development of the theory of chemical reactions in solutions

[†]This paper is to commemorate Professor Kook Joe Shin's honourable retirement.

is primarily based on its division into the theory of elementary event and the theory of reactions depending on the mobility of reactants.

By analogy with the classical Collision Theory, the theory of quasi-resonance processes is also developed the dynamic course of which (due to rather large relaxation times) is determined by the interaction Hamiltonian, not by the elementary event rate formed.^{12,13}

In constructing the theory one can also take into account that the solvent complicates the character of reactants mobility (as compared to gases) that is transformed to random walks.²⁰ It is responsible for the “cage effect”²¹ which gives rise to a new (as compared to gases) class of geminate reactions²² and complicates considerably the kinematics of “collision” of reactants in liquid solutions. It acquires the character of the encounter of reactants consisting of a sequence of re-contacts.²³ Thus the encounter means residence in the cage (in this sense the reaction at the encounter may be considered as a geminate process). That is why the kinetic theory of reactions (physicochemical processes) in solutions based on the concepts of the classical Collision Theory received the name “the Encounter Theory (ET)”.^{12,13} In the framework of the Encounter Theory the reactants do not react for the most part, as they are in the process of “free” random walks in the bulk (a reservoir of free random walks), and the reaction takes place upon their encounters the duration of which is much less than the mean time between them. Thus ET must correctly take into account all pair encounters and neglect encounters of more particles encounters.

The Encounter Theory, just as the classical Collision Theory and former theories of reactions in liquid solutions based on the concept of independent pairs, gives differential (rate) kinetic equations corresponding to the notions of independent pair encounters. The independence of pair encounters (just as the independence of pair collisions in gases) means that the contributions to the reaction kinetics from the encounters occurring at different instants of time are additive. The specific feature of the Encounter Theory in solutions, in comparison with the classical Collision Theory in gases, is a much more pronounced non-Markovian character of the theory (time dependence of rate constants) that results in the deviations²⁴⁻²⁹ from the kinetic law of mass action.³⁰ Such a non-Markovian character of the theory (i.e., time dependence of rate constant) in ET concepts (unlike non-stationary diffusion concepts in the Smoluchowski theory) is due to the incompleteness of pair encounters on the Gibbs ensemble (complete analogy with incompleteness of collisions in the classical non-Markovian Collision Theory).

Note that the independence of pair encounters also means the independence of “reservoirs” of free random walks and the encounters. If a dependence takes place, correlations accumulated during the encounters will be transferred to reactants in free random walks in the bulk, and this will inevitably result in correlations between sequential encounters.

From this point of view, the notion of independent pair

encounters in the irreversible reaction under consideration (when concentrations of both partners vary) is questionable, and at least needs substantiation. This is because the reaction course determined by the encounters changing concentrations of reactants affects the mean time of free random walks; this can give rise to a connection between “reservoirs” of encounters and free walks in the bulk. In the classical Collision Theory such a connection is weak (comparable to the contribution of triple collisions). However, in solutions, stochastic character of reactants motion (often treated as continual diffusion) is responsible for long-range space-time correlations.³¹ The reason is that for a reactant in solution one cannot say for sure whether it is in a free walks in the bulk or in the encounter with a partner (in the interval between re-contacts).

The concept of independent encounters can be examined on the basis of many-particle consideration of the reacting systems only, and the analysis of the concept for different types of irreversible reactions is the main goal of the present contribution.

Statement of the Problem

For irreversible reactions $A + A \rightarrow C$ and $A + B \rightarrow C$ the non-Markovian binary kinetic equations are of the same form both in ET and in the Waite-Smoluchowski theories

$$\frac{d[A]_t}{dt} = -K(t)[A]_t^2 \quad (2.1)$$

and

$$\frac{d[A]_t}{dt} = \frac{d[B]_t}{dt} = -K(t)[A]_t[B]_t, \quad (2.2)$$

respectively, where $K(t)$ is the non-Markovian rate constant attaining its steady value (the Markovian rate constant or steady-state constant)

$$k = \lim_{t \rightarrow \infty} K(t). \quad (2.3)$$

In this Markovian version of the theory Eqs. (2.1) and (2.2) are transformed to the equation of formal chemical kinetics corresponding to the law of mass action³⁰

$$\frac{d[A]_t^m}{dt} = -k([A]_t^m)^2 \quad (2.4)$$

and

$$\frac{d[A]_t^m}{dt} = \frac{d[B]_t^m}{dt} = -k[A]_t^m[B]_t^m. \quad (2.5)$$

Note that we used reaction rate constant for reaction $A + A \rightarrow C$ that differs twice from that used in chemical literature. It is more convenient for comparison of two considered types of reactions. Eqs. (2.4) and (2.5) give the familiar kinetics of bimolecular reactions at hand

$$[A]_t^m = \frac{[A]_0}{1 + k[A]_0 t} \quad (2.6)$$

for reaction $A + A \rightarrow C$ and

$$[A]_t^m = \frac{\Delta n \cdot [A]_0 \exp(-k\Delta nt)}{[B]_0 - [A]_0 \exp(-k\Delta nt)}; [B]_t^m = \frac{\Delta n \cdot [B]_0}{[B]_0 - [A]_0 \exp(-k\Delta nt)} \quad (2.7)$$

for reaction $A + B \rightarrow C$, where $\Delta n = [B]_t - [A]_t = [B]_0 - [A]_0$, while $[A]_0$ and $[B]_0$ are initial concentrations of reactants. For definiteness, everywhere below for the reaction $A + B \rightarrow C$ we take $[B]_0 \geq [A]_0$ ($\Delta n \geq 0$).

In the frame of ET Eqs. (2.1) and (2.2) (as Eqs. (2.4) and (2.5)) have a clear physical meaning. The product of concentrations in the right-hand side of the equations corresponds to the approach of uncorrelated particles that are in the process of free walks in the bulk, while the kinetic coefficients (rate constants) specify the efficiency of the encounter of reactants (that is the analog of collision efficiency (proportional to the cross-section of scattering in gases, if by scattering we mean chemical transformation)).

To examine the applicability of the concept of independent encounters that leads to Eqs. (2.1) and (2.2), we must derive the kinetic equation for irreversible reaction considered on the basis of many-particle consideration of the reaction systems.

If we use the many particle method for the derivation of kinetic equations based on the Waite superposition decoupling,^{9,10} we really obtain the equations considered. However it has been established that application of such an approximation to the derivation of non-Markovian binary equations of reversible reactions³²⁻³⁴ contradicts the Encounter Theory concepts when they are physically justified. The superposition approximation was criticized in a number of papers,³⁵⁻³⁸ and another approaches were developed in the literature.^{35,37-42} In the context of any of these approaches the general form of kinetic equations is convolution type integro-differential ones in accordance with the kinetic theory of chemical reactions⁴³ and non-equilibrium statistical mechanics⁴⁴

$$\frac{d[A]_t}{dt} = - \int_{-0}^t dt_0 \Sigma(t-t_0) [A]_{t_0}^2 \quad (2.8)$$

and

$$\frac{d[A]_t}{dt} = - \int_{-0}^t dt_0 \Sigma(t-t_0) [A]_{t_0} [B]_{t_0}. \quad (2.9)$$

Specific expression for the kernel (memory function) $\Sigma(t-t_0)$ should be obtained in the framework of the corresponding approach. Note that the low limit -0 in the integrals should to be used since the kernels contain $\delta(t-t_0)$ singularity at $t=0$ in their kinetic parts.⁴³

For the calculation of the kernels the method³⁷ based on the adaptation of non-stationary quantum scattering theory techniques^{45,46} and non-equilibrium statistical mechanics methods^{44,47-51} to chemically reacting systems proved to be most useful from the standpoint of the examination of the Encounter Theory concepts. This method was successfully used in the derivation of kinetic equations of a wide class of chemical reactions⁵²⁻⁶⁰ and in examining the applicability of

the concepts of the Encounter Theory.^{61,62} Now we briefly discuss the main steps of the method to show how the subsequent steps increase the accuracy of kinetic equations derived.

The method consists of several steps beginning from the many-particle statement of the problem to the final derivation of binary kinetic equations. The detailed microscopic many-particle description of the reacting system and passing to the thermodynamic limit make it possible to write hierarchies for Reduced Distribution Functions (RDF). Further derivation of the equation of corresponding reaction relies on the idea to treat the evolution of the reacting system as the evolution of space-time correlations in spatial location of reactants. The obtained hierarchies of equations for Correlation Patterns (CPs) call for closing on some level. The simplest method of such a closure is taking into consideration just two-particle correlations between reactants neglecting all three-particle ones. This approximation corresponds to the development of the so-called Integral Encounter Theory (IET) and leads to integro-differential kinetic equation. The kernel of this equation calculated using the reacting pair parameters is the basic kinetic coefficient of the theory that completely describes the encounter. However, the kinetic equation itself can be employed in a narrow time interval. To expand the applicability range of binary description, it is necessary to allow for correlation patterns of higher order than two-particle ones. Closing of a hierarchy of equations on the level of three-particle correlation patterns is implemented by extracting binary channels in the evolution of three-particle correlation patterns; this corresponds to the next step in the many-particle derivation and the development of the effective Pair Approximation (EPA). On the basis of this approximation, discarding the terms beyond the limits of binary approximation, we derive more general integro-differential equation of the Modified Encounter Theory (MET) valid over the entire time range of binary description. However, the demerit of this theory is the dependence of the kinetic coefficient (the kernel) on initial concentrations of reactants. Within the accuracy of binary approximation the kinetic equation of irreversible reaction admit further reduction to the form of rate equation (Regular form) that allows direct comparison with the Encounter Theory.

To discard the terms beyond the binary encounters approximation, the scaling procedure should be used.⁶³ The idea of the procedure is to enlarge the infinitively time-space scale and to consider the scaling system with the infinitively small concentration of reactants. This procedure that is usually used to obtain the binary kinetics from the exact kinetics calculated on the basis of many-particle consideration of the reacting system can be used on the intermediate stage of the derivation of the binary kinetic equations that considerably simplified the consideration. For example, transformation of any function $\Phi(\vec{r}^A, \vec{r}^B, t, [A], [B])$ defining the state of the pair in the initial system into the function $\tilde{\Phi}(\vec{r}^A, \vec{r}^B, t, [A], [B])$ that describes the same pair but in the scaling-system has the form

$$\tilde{\Phi}(\vec{r}_A, \vec{r}_B, t, [A], [B]) \equiv \Phi(\gamma \vec{r}_A, \gamma \vec{r}_B, \gamma^2 t, \gamma^{-2}[A], \gamma^{-2}[B]), \quad (2.10)$$

where the scaling parameter $\gamma \rightarrow \infty$. Since the encounters of three and more particles correspond to a higher order of the dilution parameter than the binary encounters it is necessary to preserve just the lowest terms in power of the parameter γ^{-1} . Then we must put $\gamma = 1$ that corresponds to the desired simplified function in the initial system.

In this contribution we use the above methods in the analysis of bimolecular irreversible reactions to refine physical concepts of the Encounter Theory. In the third section we give the description of many-particle reacting systems. In the forth and the fifth sections the kinetic equations of the Integral Encounter Theory (IET) and the Effective Pair Approximation (EPA) corresponding to different hierarchy closure levels are obtained. In the sixth section one can find the non-Markovian binary equations of the Modified Encounter Theory (MET). In Section 7 the kinetic equations in the final Regular Form (RF) are deduced and compared with ET equations. Principal results of the work are given in the Summary.

Description of the Reacting System

In the many-particle description of the irreversible reacting systems $A + A \rightarrow C$ and $A + B \rightarrow C$ we restrict ourselves to the consideration of spatially homogeneous systems, and first we neglect the initial correlations and the force interactions between reactants considering them as a point particles thus concentrating on the manifestation of chemical correlations. Besides, for simplicity, by configuration space coordinates q we mean space coordinates of reactants.

Then their free motion in a continual medium is defined by the Markovian process of random walks occurring in the general case by random jumps of a finite length. Such a motion is specified by the integral operator \hat{L}_α , where α denotes the species of reactants, A or B . The elementary rate of the irreversible reaction at hand is defined by the rate $w(A_i - B_j)$ depending on the relative-position vector $\vec{r} = A - B$, where A_i and B_j are the coordinates of the i -th reactant of A species and the j -th reactant of B species, respectively.

In our mathematical description, we shall use the extended time interval $-\infty < t < \infty$. At $t < 0$ the values of all functions are taken equal to zero, and at $t > 0$ these values coincide with physical quantities. The functions are obtained by multiplication of initial functions by the stepwise Heaviside function $\theta(t)$. So differential equations do not require that the initial conditions be stated. They are taken into account by introducing δ -functional source in the right-hand side of appropriate differential equation. This makes it possible to consider space and time variables on equal terms which is necessary for the introduction of integral operators acting on the functions of space-time variables, and simplifying significantly the intermediate calculations. Besides, for simplicity, further we shall denote the time derivative on the extended time interval as ∂_t . In such a formalism the reaction operator \hat{v}_f for any of the reactions considered has

the kernel

$$v_f(\vec{r}, t | \vec{r}_0, t_0) = -w(\vec{r}) \delta(\vec{r} - \vec{r}_0) \delta(t - t_0). \quad (3.1)$$

In the framework of such approach the general many-particle method applied to the description of irreversible reactions $A + A \rightarrow C$ and $A + B \rightarrow C$ ^{37,38,61,62} allows to write equations for the variation of A species concentration that are defined by the lowest order equations of the hierarchy for Correlation Patterns for the reaction $A + A \rightarrow C$

$$\partial_t [A]_t = \delta(t) [A]_0 + \int d\vec{r} \hat{v}_f [A]_t^2 + \int d\vec{r} \hat{v}_f \pi_{AA}(\vec{r}, t) \quad (3.2)$$

and for the reaction $A + B \rightarrow C$

$$\partial_t [A]_t = \delta(t) [A]_0 + \int d\vec{r} \hat{v}_f [A]_t [B]_t + \int d\vec{r} \hat{v}_f \pi_{AB}(\vec{r}, t). \quad (3.3)$$

Concentration variation rate of B reactants has a similar form. The first terms in the right-hand sides of Eqs. (3.2) and (3.3) are responsible for taking account of the initial conditions, and the second terms describe the contribution from uncorrelated encounter of two A reactants or A and B reactants to the reaction rate. Accordingly, the third terms describe the contributions from correlation in the position of the same reactants which is specified by the correlation patterns $\pi_{AA}(\vec{r}, t)$ or $\pi_{AB}(\vec{r}, t)$. In the general case these patterns should be found from the closed set of equations derived from the hierarchy for Correlation Patterns of the reacting systems by the decoupling procedure that can be performed on any hierarchy closure level.^{37,62,63}

The Integral Encounter Theory (IET)

The simplest method of hierarchy closure is to take only pair correlations into consideration neglecting the evolution of any three-particle Correlation Patterns in the infinite hierarchy. CPs of AA in Eq. (3.2) or AB in Eq. (3.3) reactants for the reactions $A + A \rightarrow C$ or $A + B \rightarrow C$ hereinafter denoted in this approximation as $\pi_{AA}^e(\vec{r}, t)$ and $\pi_{AB}^e(\vec{r}, t)$, respectively, obey similar closed equations

$$(\partial_t - \hat{L}_{AA} - \hat{v}_f) \pi_{AA}^e(\vec{r}, t) = \hat{v}_f [A]_t^2 \quad (4.1)$$

and

$$(\partial_t - \hat{L}_{AB} - \hat{v}_f) \pi_{AB}^e(\vec{r}, t) = \hat{v}_f [A]_t [B]_t \quad (4.2)$$

that differ from one another by relative motion and concentrations of the encountering reactants.

Due to such a radical simplification of the equations for two-particle CPs, their mathematical structure is easy to find. Really, the solutions of both of these equations have the following form in the Green function formalism

$$\pi_{AA}^e(\vec{r}, t) = \hat{g}_{AA} \hat{v}_f [A]_t^2 \quad (4.3)$$

and

$$\pi_{AB}^e(\vec{r}, t) = \hat{g}_{AB} \hat{v}_f [A]_t [B]_t, \quad (4.4)$$

where \hat{g}_{AA} and \hat{g}_{AB} are the propagators of the pairs AA or AB the kernels of which are the probability densities to find the reactants in the position \vec{r} at the moment t if it was \vec{r}_0 at the moment t_0 . These kernels obey similar equations for both

reactions

$$(\partial_t - \hat{\mathcal{L}}_{AA} - \hat{v}_f)g_{AA}(\vec{r}, t|\vec{r}_0, t_0) = \delta(\vec{r} - \vec{r}_0)\delta(t - t_0) \quad (4.5)$$

or

$$(\partial_t - \hat{\mathcal{L}}_{AB} - \hat{v}_f)g_{AB}(\vec{r}, t|\vec{r}_0, t_0) = \delta(\vec{r} - \vec{r}_0)\delta(t - t_0). \quad (4.6)$$

On substitution of solution (4.3) in equation (3.2), and solution (4.4) in equation (3.3) we have the desired kinetic equations of the Integral Encounter Theory (IET) that are integro-differential equations of the form of Eqs. (2.8) and (2.9) (in the extended time interval) with similar kernels (memory functions)

$$\Sigma(t - t_0) \equiv \Sigma^e(t - t_0) = -\int d\vec{r} d\vec{r}_0 t(\vec{r}, t - t_0|\vec{r}_0, 0). \quad (4.7)$$

Here $t(\vec{r}, t - t_0|\vec{r}_0, 0)$ is so called t -matrix

$$t(\vec{r}, t - t_0|\vec{r}_0, 0) = -w(\vec{r})\delta(\vec{r} - \vec{r}_0)\delta(t - t_0) + w(\vec{r})g(\vec{r}, t|\vec{r}_0, t_0)w(\vec{r}_0). \quad (4.8)$$

We see from Eq. (4.8) that kernel (4.7) of kinetic equations really contains the kinetic part with $\delta(t - t_0)$ singularity and relaxing part (depending on the mobility of reactants). We can see that t -matrix is the kernel of T -operator defined as

$$\hat{t} = \hat{v}_f + \hat{v}_f \hat{g} \hat{v}_f, \quad (4.9)$$

where \hat{g} is any of the propagators \hat{g}_{AA} or \hat{g}_{AB} (for the corresponding reaction). It is obvious that T -operator and t -matrix are the analogs⁶⁴ of the corresponding objects of the non-stationary quantum scattering theory,^{45,46} and this is natural since the encounter in solutions is a prototype of collision in gases. Thus the memory functions $\Sigma^e(t - t_0)$ that for both reactions considered are expressed in terms of the averaged evolution of the reaction pairs AA or AB completely describe a pair (binary) encounter of the corresponding reactants. That is why IET is a binary theory, however, further we shall show that it fails to completely allow for the contribution of all binary encounters in concentration variation and thus has an unjustifiably narrow time interval of validity.^{25,65}

Nevertheless, it can be shown that the non-Markovian IET reduces to the Markovian theory (that corresponds to the kinetic law of mass action of the formal chemical kinetics). For this purpose, it should be taken into account that the characteristic time scale of the kernel decay $\Sigma^e(t - t_0)$ is of the order of pair encounter duration of reactants in solution, i.e., it has a microscopic time scale. In the zero approximation one can put pair encounter duration zero, and use δ -shaped approximation for the kernel $\Sigma^e(t - t_0)$ (as scaling shows²⁵)

$$\Sigma^e(t) \cong k\delta(t), \text{ where } k = \int_{-\infty}^{\infty} dt \Sigma^e(t). \quad (4.10)$$

As a result, the non-Markovian equations (2.8) and (2.9) are reduced to the Markovian equations (2.4) and (2.5) with the reaction rate constant (see Eqs. (4.10))

$$k = -\int d\vec{r} d\vec{r}_0 t^s(\vec{r}|\vec{r}_0), \text{ where } t^s = \int_{-\infty}^{\infty} dt \hat{t} = \lim_{s \rightarrow 0} \hat{t}^s(s). \quad (4.11)$$

Here the upper index s denotes the steady-state value of the T -operator, and the upper index L is its Laplace transform depending on the Laplace variable s . The obtained relation between the Markovian (steady-state) rate constant and stationary T -operator makes it possible to easily form the T -matrix recipe for the calculation of the rate constant k in the frame of stationary statement of the pair problem.

Besides in IET applicability range the integro-differential kinetic equations (2.8) and (2.9) may be brought into the form of differential equations (2.1) and (2.2) of the Encounter Theory (ET). With this aim, in the time convolution one should neglect the change in concentrations of A and B reactants in the characteristic variation range of the kernel Σ^e putting $[A]_{t_0} \cong [A]_t$ and $[B]_{t_0} \cong [B]_t$. Then equations (2.8) and (2.9) give IET kinetic equations in the desired differential forms (2.1) and (2.2) of the Encounter Theory, where the non-Markovian rate constant $K(t)$ is introduced

$$K(t) = \int_{-\infty}^t d\tau \Sigma^e(\tau) = -\int_{-\infty}^t d\tau \int d\vec{r} d\vec{r}_0 t(\vec{r}, \tau|\vec{r}_0, 0). \quad (4.12)$$

It is a direct generalization of the definition of the Markovian rate constant (4.11).

The Effective Pair Approximation (EPA) and the Modified Encounter Theory (MET)

The restricted time interval of the validity of the derived kinetic equations indicates that the Integral Encounter Theory (IET) fails to correctly allow for long-term transformations of two-particle Correlation Patterns, since it ignores the reaction with particles in the bulk. To take them into account, we must close hierarchies on a higher level. Really, applying the currently existing method for many-particle derivation of kinetic equations based on the extraction of binary channels from the evolution of three-particle Correlation Patterns³⁷ to the consideration of the reaction $A + A \rightarrow C$, we can obtain the equation for the evolution of CP of some effective pair⁶¹

$$(\partial_t - \hat{\mathcal{L}}_{AA} - \hat{v}_f + 4k[A]_t^2)\pi_{AA}(\vec{r}, t) = \hat{v}_f[A]_t^2 \quad (5.1)$$

and the equation for the evolution of some uncorrelated effective pairs for the reaction $A + B \rightarrow C$ ⁶²

$$\begin{cases} \{\partial_t - \hat{\mathcal{L}}_{AB} - \hat{v}_f + k([A]_t + [B]_t)\}\pi_{AB}(\vec{r}, t) \\ = \hat{v}_f[A]_t[B]_t - k([A]_t\pi_{BB}(\vec{r}, t) + [B]_t\pi_{AA}(\vec{r}, t)) \\ (\partial_t - \hat{\mathcal{L}}_{AA} + 2k[B]_t)\pi_{AA}(\vec{r}, t) = -2k[A]_t\pi_{AB}(\vec{r}, t), \\ (\partial_t - \hat{\mathcal{L}}_{BB} + 2k[A]_t)\pi_{BB}(\vec{r}, t) = -2k[B]_t\pi_{AB}(\vec{r}, t). \end{cases} \quad (5.2)$$

The operators $\hat{\mathcal{L}}_{AB}$, $\hat{\mathcal{L}}_{AA}$, and $\hat{\mathcal{L}}_{BB}$ specify the translational motion in the space of relative coordinates of the pairs of AB , AA , and BB reactants, respectively. Note that similar equations were also proposed in the literature in the framework of heuristic approach.⁶⁶

We see that in contrast to IET, in the frame of which the evolutions of pair correlations are the same for both types of reactions $A + A \rightarrow C$ and $A + B \rightarrow C$, the evolutions of the effective pairs for these two types of reactions drastically

differ.

For the reaction $A + A \rightarrow C$ it is the evolution of one chemically interacting effective pair that decays due to the translational motion of reactants and their chemical interactions with the same reactants at encounters and in the bulk. Note that the decay of the Correlation Pattern due to the interaction with the bulk reactants proceeds in half the time (at the rate $4k[A]_t$) than the corresponding decay of concentrations $[A]_t^2$ in the bulk (at the rate $2k[A]_t$) due the pair encounters. We can see that the solution of Eq. (5.1) differs from solution (4.3) of Eq. (4.1) only by the exponential factor $\exp(-4k \int_{t_0}^t d\tau [A]_\tau^m)$. Within the accuracy of the binary theory, in this exponential factor we can replace the kinetics $[A]_t$ by its Markovian kinetics $[A]_t^m$. Thus we immediately obtain from Eq. (3.2) the final kernel of binary kinetic equation (2.8) of the reaction $A + A \rightarrow C$ valid (unlike IET) over the entire time interval of binary kinetics

$$\Sigma(t|t_0) = \Sigma^e(t-t_0) \exp(-4k \int_{t_0}^t d\tau [A]_\tau^m). \quad (5.3)$$

It is seen that the kernel derived is the modification of IET kernel (that contains complete information about the encounter) by multiplying it by the factor that depends on steady-state (Markovian) reaction constant (that, in turn, apart from initial concentration, is determined by IET kernel itself (see Eq. (4.10))). That is why the approximation thus constructed for the reaction $A + A \rightarrow C$ is called the Modified Encounter Theory (MET). By identity transformation, this kernel can be rewritten in an equivalent form

$$\Sigma(t-t_0) = \Sigma^e(t-t_0) \exp(-2k \int_{t_0}^t d\tau [A]_\tau^m) + \Lambda_{AA}(t|t_0), \quad (5.4)$$

where

$$\Lambda_{AA}(t|t_0) = e^{-2k \int_{t_0}^t d\tau [A]_\tau^m} \left(e^{-2k \int_{t_0}^t d\tau [A]_\tau^m} - 1 \right) \Sigma^e(t-t_0). \quad (5.5)$$

In this representation the first term in r.h.s of Eq. (5.4) is the product of IET kernel that describes the reaction dynamics at the encounter and the Markovian reaction kinetics ($[A]_t^m/[A]_{t_0}^m = \exp(-2k \int_{t_0}^t d\tau [A]_\tau^m)$) that describes the macroscopic reaction dynamics (in the time interval from t_0 to t) in the bulk. It corresponds to the independence of these two dynamics. Thus the second term in r.h.s of Eq. (5.4) $\Lambda_{AA}(t|t_0)$ (5.5) describes macroscopic correlation between these two dynamics. Calculation of this correlation term (5.5) with allowance only for the leading term of the expansion in the scaling parameter (sufficient in the binary theory) permits the use of IET memory function on meso- and macroscales²⁵

$$\Sigma^e(\tau) \cong \Sigma_p^e(\tau) = k\delta(\tau) + \frac{k^2}{4(\pi\bar{D}_{AA})^{3/2}} \partial_\tau \frac{\Theta(\tau)}{\sqrt{\tau}}, \quad (5.6)$$

where \bar{D}_{AA} is the relative macrodiffusion coefficient of A reactants. The first term of this approximation corresponds to the Markovian approximation (4.10) and is the leading term of the expansion in the scaling parameter. The second

non-Markovian term corresponds to the next order of this parameter. Since the contribution from the Markovian term in Eq. (5.5) is equal to zero, the leading non-zero term in Eq. (5.5) is determined by the second (non-Markovian) term in expression (5.6). Thus $\Lambda_{AA}(t|t_0)$ depends only on macroparameters (k , \bar{D}_{AA} and initial concentration) as should be.

However, accumulation of macroscopic correlations is more complicated for the reaction $A + B \rightarrow C$ when the subsequent evolution of three interrelated correlation patterns takes place. It leads to the decay of CP π_{AB} of the reacting pair not only due to the translational motion of reactants and their chemical interactions with each other and with reactants in the bulk, but due to the transformation of different Correlation Patterns into each other. Two of CPs are Correlation Patterns of chemically not interacting identical particles. Generally speaking, such a transformation of CPs can occur not only on the immediate approach of reactants (at binary encounter times), but also at rather large times, when reactants A and B are separated by meso- and macro-distances, however, correlation between them persists. Additional transformation of all CPs is due to reaction with particles in the bulk. Thus macroscopic correlations of both reacting particles and non-reacting species of the same type are accumulated in the system. This inevitably affects the evolution of the Correlation Pattern π_{AB} defining, according to Eq. (3.3), chemical conversion rate. The derived set of EPA equations is rather intricate. In solving it, one should take into consideration that the evolution of the CP π_{AB} is not governed solely by the evolution π_{AB}^e of independent reacting particle (as in IET), i.e., EPA is not the binary theory. For some reactions this approximation can describe fluctuation tails of the kinetics realized beyond the limits of the binary theory.⁶⁶ Thus to obtain the desired solution, one has to extract the binary evolution from the evolution of two-particle correlation patterns of EPA. Apart from replacing the kinetics $[A]_t$ and $[B]_t$ by their Markovian kinetics $[A]_t^m$ and $[B]_t^m$ in Eqs. (5.2) some mathematical tricks and application of the scaling procedure are required to obtain the desired solution. As a result we obtain the final kernel of binary kinetic equation (2.9) of the reaction $A + B \rightarrow C$ valid (in contrast to IET) over the entire time interval of the binary kinetics

$$\Sigma(t|t_0) = \Sigma^e(t|t_0) \exp(-k \int_{t_0}^t d\tau ([A]_\tau^m + [B]_\tau^m)) + \Lambda_{AB}(t|t_0), \quad (5.7)$$

where

$$\Lambda_{AB}(t|t_0) = -k^2 (g_{eff}^D(0, t|0, t_0) - g_{AB}^D(0, t|0, t_0) \exp(-k \int_{t_0}^t d\tau ([A]_\tau^m + [B]_\tau^m))). \quad (5.8)$$

Here $g_{AB}^D(0, t|0, t_0)$ is macrodiffusion free propagator (in absence of reaction) that obeys Eq. (4.6) at $\hat{v}_f \equiv 0$, and $\hat{\mathcal{L}}_{AB} = \bar{D}_{AB} \Delta_{\vec{r}}$,

$$g_{AB}^D(0, t|0, t_0) = \frac{\Theta(t-t_0)}{(4\pi\bar{D}_{AB}(t-t_0))^{3/2}} \quad (5.9)$$

and $g_{eff}^D(\vec{r}, t|\vec{r}_0, t_0) \equiv (g_{eff}^D)_{11}(\vec{r}, t|\vec{r}_0, t_0)$ is the corresponding matrix

element of the free propagator of the effective pair that obeys the matrix equation

$$\left(\partial_t - \Delta_{\vec{r}} \begin{pmatrix} \bar{D}_{AB} & 0 & 0 \\ 0 & \bar{D}_{AA} & 0 \\ 0 & 0 & \bar{D}_{BB} \end{pmatrix} + k \begin{pmatrix} [A]_t^m + [B]_t^m & [B]_t^m & [A]_t^m \\ 2[A]_t^m & 2[B]_t^m & 0 \\ 2[B]_t^m & 0 & 2[A]_t^m \end{pmatrix} \right) \mathbf{g}_{eff}^D(\vec{r}, t | \vec{r}_0, t_0) = \delta(\vec{r} - \vec{r}_0) \delta(t - t_0) \mathbf{E}_3, \quad (5.10)$$

where \bar{D}_{AB} , \bar{D}_{AA} and \bar{D}_{BB} are relative macrodiffusion coefficients, and \mathbf{E}_3 is a three-dimension unity matrix.

Eq. (5.7) similar to Eq. (5.4) contains two terms the first of which describes independent reaction dynamics at the encounter and in the bulk $\left(\frac{[B]_t^m [A]_t^m}{[B]_0^m [A]_0^m} = \exp(-k \int_{t_0}^t d\tau ([A]_{\tau}^m + [B]_{\tau}^m)) \right)$, and the second term describes correlation between the dynamics. Thus we see that the derived kernel (5.7) can be formed using IET kernel that contains complete microscopic information about the encounter and the knowledge of the macroscopic kinetic parameters (the Markovian rate constant, relative macrodiffusion coefficients of reactants and initial concentrations). Thus it is really the Modified Encounter Theory (MET).

Calculation of the free propagator of the effective pair is the most difficult part in the construction of MET kernel (to be more exact, in the calculation of the correlation part Λ_{AB}), and will be presented in this paper for the case of equal macrodiffusion coefficients of the species $\bar{D}_A = \bar{D}_B$.

However, when B reactant is in excess, it is possible to pass to the limit in Eqs. (5.7), (5.8), and (5.10)

$$[A]_t^m \rightarrow 0; [B]_t^m = [B] = \text{const.} \quad (5.11)$$

In this case

$$g_{eff}^D = g_{AB}^D \exp(-k[B](t - t_0)) \quad (5.12)$$

and $\Lambda_{AB}(t|t_0) = 0$. Then MET memory function (5.7) reduces to the familiar expression^{38,66}

$$\Sigma(t|t_0) = \Sigma^e(t|t_0) \exp(-k[B](t - t_0)), \quad (5.13)$$

corresponding to the independent dynamics.

Regular Form of MET Kinetic Equations (The Generalized Encounter Theory (GET))

Equations of the Modified Encounter Theory (MET) derived are the final form of integrodifferential binary kinetic equations valid over the entire time range of binary kinetics. However, for irreversible reactions considered they can be transformed into an equivalent differential form (Regular form that is more familiar to chemists) using the time shift rule^{37,54} valid within the accuracy of binary encounter approximation. For the reactions $A + A \rightarrow C$ and $A + B \rightarrow C$ they are

$$[A]_t \Rightarrow \exp(-k \int_{t_0}^t d\tau [A]_{\tau}^m) [A]_{t_0} \quad (6.1)$$

and

$$[A]_t \Rightarrow \exp(-k \int_{t_0}^t d\tau [B]_{\tau}^m) [A]_{t_0}; [B]_t \Rightarrow \exp(-k \int_{t_0}^t d\tau [A]_{\tau}^m) [B]_{t_0}, \quad (6.2)$$

respectively. They differ from the identities that follow from the non-Markovian kinetic equations (2.1) and (2.2) in that equations (6.1) and (6.2) involve the exact kinetics $[A]_t$, $[A]_{t_0}$, $[B]_t$, and $[B]_{t_0}$ at different moments of time but the kinetics in the interval $[t, t_0]$ are approximated by the Markovian kinetics.

As a result, the initial MET equations take a Regular Form of differential kinetic equations. For the reaction $A + A \rightarrow C$ we obtain

$$\frac{d[A]_t}{dt} = -K(t)[A]_t^2 + J_{AA}(t) \quad (6.3)$$

with the source

$$J_{AA}(t) = - \int_{t_0}^t dt_0 \Lambda_{AA}(t|t_0) ([A]_{t_0}^m)^2 \\ \equiv ([A]_t^m)^2 \int_{t_0}^t dt_0 \Sigma_p^e(t|t_0) (1 - \exp(-2k \int_{t_0}^t d\tau [A]_{\tau}^m)) \quad (6.4)$$

and for the reaction $A + B \rightarrow C$

$$\frac{d[A]_t}{dt} = -K(t)[A]_t[B]_t + J_{AB}(t) \quad (6.5)$$

with the source

$$J_{AB}(t) = - \int_{t_0}^t dt_0 \Lambda_{AB}(t|t_0) [A]_{t_0}^m [B]_{t_0}^m \equiv [A]_t^m [B]_t^m k^2 \\ \int_{t_0}^t dt_0 (g_{eff}^D(0, t|0, t_0) \exp(k \int_{t_0}^t d\tau ([A]_{\tau}^m + [B]_{\tau}^m)) - g_{AB}^D(0, t|0, t_0)). \quad (6.6)$$

Note that in the calculations of the sources (6.4) and (6.6) we used Markovian kinetics $[A]_{t_0}^m$ and $[B]_{t_0}^m$ that is possible within binary theory accuracy. It is seen that the extension of the time validity range of the kinetic equations achieved in MET not only widens the time applicability range of differential equations of the Encounter Theory derived from IET but discovers additional inhomogeneous sources. The kinetic equations of a such structure are known in the theory of irreversible chemical reactions,¹⁰ but the sources take into account initial space correlations in many-particle systems. However, the presence of the sources $J_{AA}(t)$ or $J_{AB}(t)$ in Eqs. (6.3) and (6.5) are not related to initial space correlations, since they are equal to zero at the initial moment of time. Written in the forms

$$\frac{d[A]_t}{dt} = -K(t) \{ [A]_t^2 + \Pi_{AA}^{macro}(t) \} \quad (6.7)$$

and

$$\frac{d[A]_t}{dt} = -K(t) \{ [A]_t[B]_t + \Pi_{AB}^{macro}(t) \} \quad (6.8)$$

with initial conditions $[A]_{t=0} = [A]_0$ and $[B]_{t=0} = [B]_0$. Eqs. (6.7) and (6.8) show the presence of macroscopic correlations of reactants in the process of free random walks in the bulk. Thus the encounters in dilute solutions (except the case of B reactants in excess in the reaction $A + B \rightarrow C$) are dependent in contrast to collisions in gases. The Encounter

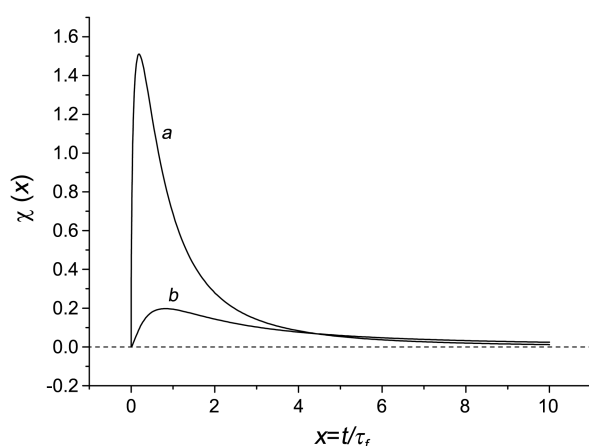


Figure 1. Time behaviour of functions $\chi_{AA}(x)$ Eq. (6.11) (curve a) and $\chi_{AB}(x)$ (curve b) Eq. (6.14).

Theory taking account of dependent encounters can be considered as the Generalized Encounter Theory (GET).

The macroscopic correlations are described by the correlation patterns

$$\Pi_{AA}^{macro}(t) \cong -\frac{J_{AA}(t)}{k} \equiv [A]_0^2 P_{AA}^{macro}(t) \quad (6.9)$$

and

$$\Pi_{AB}^{macro}(t) \cong -\frac{J_{AB}(t)}{k} \equiv [A]_0[B]_0 P_{AB}^{macro}(t). \quad (6.10)$$

Note that when transforming sources (6.4) and (6.6) in Eqs. (6.3) and (6.5) into the correlation patterns in Eqs. (6.7) and (6.8), we put $K(t) \cong k$, which is possible within the required accuracy.

Now consider the reaction $A + B \rightarrow C$ in the case of equal mobilities of species A and B (is this case $\bar{D}_{AA} = \bar{D}_{AB} = \bar{D}$) and equal initial concentrations $[A]_0 = [B]_0$ that are equal to the concentration of species A in the reaction $A + A \rightarrow C$. In this case, in the framework of the Encounter Theory (and the formal chemical kinetics), the kinetics of both reactions $A + A \rightarrow C$ and $A + B \rightarrow C$ (at equal elementary event rates) are the same. However, manifestations of macroscopic correlations are absolutely different. Really, the quantity $P_{AA}^{macro}(t)$ in the correlation pattern $\Pi_{AA}^{macro}(t)$ is⁶¹

$$P_{AA}^{macro}(t) = \varepsilon \chi_{AA}(k[A]_0 t),$$

$$\varepsilon = \frac{k^{3/2} \sqrt{[A]_0}}{12(\pi \bar{D})^{3/2}}; \quad \chi_{AA}(k[A]_0 t) = \sqrt{k[A]_0 t} \frac{6 + 5k[A]_0 t}{(1 + k[A]_0 t)^4} \quad (6.11)$$

and demonstrates the time behaviour shown in Figure 1(a).

For reaction $A + B \rightarrow C$ in this case solution to Eq. (5.10) (at $[A]_t^m = [B]_t^m$)⁶² is

$$g_{eff}^D(0, t|0, t_0) = g_{AB}^D(0, t|0, t_0) \frac{1}{2} (1 + \exp(-4k \int_{t_0}^t d\tau [A]_\tau^m)) \quad (6.12)$$

and from Eq. (6.6) we have

$$J_{AB}(t) = 2([A]_t^m)^2 k^2 \int_{t_0}^t dt_0 g_{AB}^D(0, t|0, t_0) \sinh^2(k \int_{t_0}^t d\tau [A]_\tau^m). \quad (6.13)$$

Then from Eqs. (2.6), (5.9) and the definition $P_{AB}^{macro}(t) = \varepsilon \chi_{AB}(x)$, where $x = k[A]_0 t$ we obtain the quantity⁶²

$$\chi_{AB}(x) = -\frac{9(1+x)^{3/2} \ln(\sqrt{x} + \sqrt{1+x}) + \sqrt{x}(3x^2 - 4x - 9)}{4(1+x)^4} \quad (6.14)$$

that demonstrates the time behaviour shown in Figure 1(b).

It is seen that accumulation of macroscopic correlations in the reservoir of free walks of reactants in the bulk due to their encounters for the reaction of identical particles $A + A \rightarrow C$ occurs at characteristic mesotimes: $(0.19 \tau_f)$ while for the reaction of different particles $A + B \rightarrow C$ it proceeds slower $(0.8 \tau_f)$. However, the most drastic difference is that correlation patterns for the reactions considered are of the opposite sign. For the reaction $A + A \rightarrow C$ macroscopic correlations accelerate the reaction, but for the reaction $A + B \rightarrow C$ they inhibit it.

Then after the attainment their maximum values the macroscopic correlations decay due to the encounters and disappear at all at large times. The time $\tau_f = (k[A]_0)^{-1}$ may be identified with the mean time between sequential encounters of reactants (it is the analog of a free pass time in gas phase reactions). The times of the order of τ_f are macroscopic. Nevertheless, macroscopic correlations affect the non-Markovian tails of the kinetics. Figure 2 shows the non-Markovian part of GET kinetics in relative units (relative deviation of the non-Markovian GET from the Markovian one) for the parameter value $\varepsilon = 0.067$ depending on the dimensionless time $x = k[A]_0 t = t/\tau_f$

$$\Delta(x) = \frac{[A]_t - [A]_t^m}{[A]_t^m}. \quad (6.15)$$

The Influence of the force Interactions and the Decay of Reactants on Macroscopic Correlations

The force interactions between reactants (and products) give rise to additional correlations that affect the reactions course. To take them into account, note that the influence of the force interactions in the framework of the Encounter Theory based on the conception of independent pair encounters is physically evident. Really these interactions should be allowed for just in the reacting pairs of the encountering particles A with A and A with B only, since the influence of the interactions of the reacting pairs AA or AB with other particles (including products C) are insignificant in the ET making allowance for two-particles encounters only. Since force interactions make influence on the relative motion in the corresponding reacting pair they should be included in the operator \hat{L} of the relative motion of the corresponding pairs or in the propagator \hat{g} in Eqs. (4.8) and (4.9) thus changing in the well-known manner the kinetic coefficients $\Sigma^e(t)$, k or $K(t)$ of IET or ET.

However, even at small density parameters, taking into account the above force interactions in the more general GET theory (in calculation of the source terms) that considers the dependence of pair encounters of reactants in solution determined by the contribution of three-particle

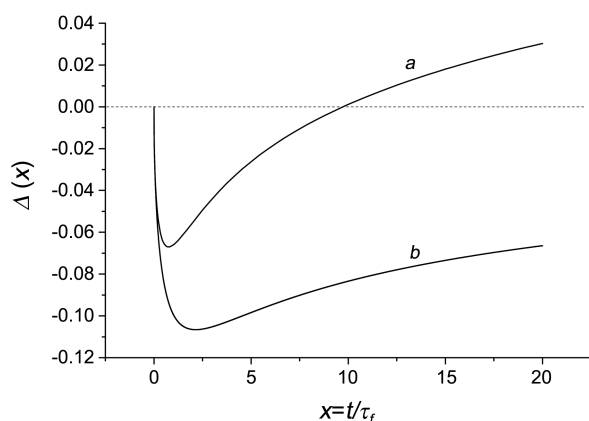


Figure 2. Time behaviour of the relative deviation (6.15) of the non-Markovian GET kinetics from the Markovian one (2.7) for $\varepsilon = 0.067$: curve a -for kinetics GET of reaction $A + B \rightarrow C$ obeying Eq. (6.5); curve b -for kinetics GET of reaction $A + A \rightarrow C$ obeying Eq. (6.3).

correlations into the kinetics is not so apparent. In this case the interactions of reactants with each other and with product particles C can, in principle, affect the accumulation of macroscopic correlations. Nevertheless, some physical arguments can be used to answer the question. Really, as it seen from the foregoing, macroscopic correlations are essential on meso-or macroscopic time-space scale depending on macroscopic kinetic parameters only. Thus microscopic evolution determines only these parameters and additional influence of microscopic force interactions on the considered macro-scale can hardly take place. Exact consideration including the force interaction in many-particle model of $A + A \rightarrow C$ reaction from the very beginning supports the given arguments.⁶¹ Exact consideration of the corresponding model for the reaction $A + B \rightarrow C$ will be done elsewhere.

Let us consider reaction $A + A \rightarrow C$ of nonstable reactants A with lifetime τ_A . Since the decay of reactants in the irreversible reactions considered does not influence on the reaction rate constant $K(t)$ and k (as is seen from further consideration) the Markovian kinetic equation is

$$\frac{d[A]_t^m}{dt} = -[A]_t^m / \tau_A - k([A]_t^m)^2 \quad (7.1)$$

and gives

$$[A]_t^m = \frac{[A]_0}{\tau_A k [A]_0 \exp(t/\tau_A) - \tau_A k [A]_0 + \exp(t/\tau_A)} \quad (7.2)$$

Equation EPA for the Correlation Pattern $\pi_{AA}(\vec{r}, t)$ can be written as

$$(\partial_t - \hat{\mathcal{L}}_{AA} - \hat{v} + 4k[A]_t + 2/\tau_A)\pi_{AA}(\vec{r}, t) = \hat{v}[A]_t^2 \quad (7.3)$$

and differs from Eq. (5.1) by additional term on l.h.s. Then the kernel of integro-differential MET kinetic equation differs from Eq. (5.3) by additional exponential factor only

$$\Sigma(t|t_0) = \Sigma^e(t-t_0) \exp\left(-4k \int_{t_0}^t d\tau [A]_\tau^m - 2 \frac{t-t_0}{\tau_A}\right) \quad (7.4)$$

as every term in representation (5.4) and expression (5.5). Using now new time shift rule

$$[A]_t \Rightarrow [A]_{t_0} \exp(-(t-t_0)/\tau_A - k \int_{t_0}^t d\tau [A]_\tau^m) \quad (7.5)$$

we obtain

$$\frac{d[A]_t}{dt} = -K(t)[A]_t^2 - [A]_t / \tau_A + J_{AA}(t) \quad (7.6)$$

with the previous definition (4.12) of non-Markovian reaction rate constant and definition of inhomogeneous source by the second of Eqs. (6.4), where new Markovian kinetics (7.2) instead of kinetics (2.6) should to be used. Then for $\chi_{AA}(k[A]_0 t) \equiv \phi_{AA}(y)$, where $y = \eta x = k[A]_0 \eta t$ we obtain

$$\chi_{AA}(k[A]_0 t) \equiv \phi_{AA}(y) = 3 \exp(-2y) \eta^{5/2} \frac{2(1+\eta)f(y) - \sqrt{2}f(y\sqrt{2})}{(1+\eta - \exp(-y))^4}, \quad (7.7)$$

where we introduce parameter $\eta = (k[A]_0 \tau_A)^{-1}$ and function

$$f(y) = \exp(-y) \int_0^{\sqrt{y}} \frac{\exp(\tau^2) - 1}{\tau^2} d\tau = -\frac{1}{\sqrt{y}} (1 - \exp(-y)) + 2w(\sqrt{y}). \quad (7.8)$$

Here

$$w(y) = \exp(-y^2) \int_0^y \exp(\tau^2) d\tau = -\frac{\sqrt{\pi}}{2} \exp(-y^2) (iy \Phi(iy)) \quad (7.9)$$

is Doson integral⁶⁷ and $\Phi(iy)$ is error function of imaginary argument. Using that

$$w(y) \cong \begin{cases} y(1-y^2/3), & y \ll 1 \\ \frac{1}{2y} \left(1 + \frac{1}{2y^2}\right), & y \gg 1 \end{cases} \quad f(y) \cong \begin{cases} \sqrt{y}(1-5y/6), & y \ll 1 \\ \frac{1}{2} y^{-3/2}, & y \gg 1 \end{cases} \quad (7.10)$$

we obtain from Eq. (7.7) at $y = k[A]_0 \eta t \ll 1$ expression for $\chi_{AA}(k[A]_0 t)$ that coincides with the corresponding expression in Eqs. (6.11). At $\eta \rightarrow 0$ (absence of reactants decay) as it should be. But the most surprising is the fact that the expression just derived at $k[A]_0 \eta t \ll 1$ is valid at arbitrary η values. It means that at the initial stage the reactants decay does not influence on the accumulation of macroscopic correlations and induces additional decay of macroscopic correlations at sufficiently large times only. At $k[A]_0 \eta t \gg 1$ we obtain from Eqs. (7.10) and (7.7)

$$\chi_{AA}(k[A]_0 t) \cong \frac{\eta \left(\frac{3}{4} + \eta\right)}{(1+\eta)^4 (k[A]_0 t)^{3/2}} \exp(-2k[A]_0 \eta t). \quad (7.11)$$

Note that apart from the exponential decay due to reactants non stability additional power law decay $(k[A]_0 t)^{-3/2}$ due to encounters takes place. However this power law does not coincide with corresponding power law $(k[A]_0 t)^{-5/2}$ for stable reactants (see Eq. (6.11)), i.e. demonstrates slower power decay. As a consequence at $\eta = 0$ asymptotic term considered vanishes and one must calculate the next one.

The time behaviour of $\chi_{AA}(k[A]_0 t)$ (7.7) is shown in Figure 3.

Consider now reaction $A + B \rightarrow C$ of nonstable reactants A and B with lifetimes τ_A and τ_B , respectively, for which EPA

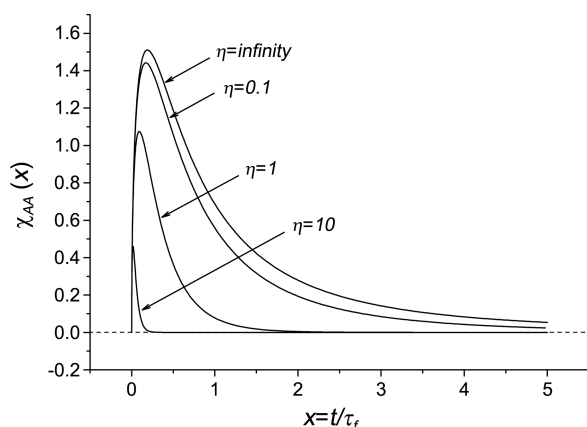


Figure 3. Time behaviour of functions $\chi_{AA}(x)$ (7.7) for different values of $\eta = \tau_f/\tau_A$.

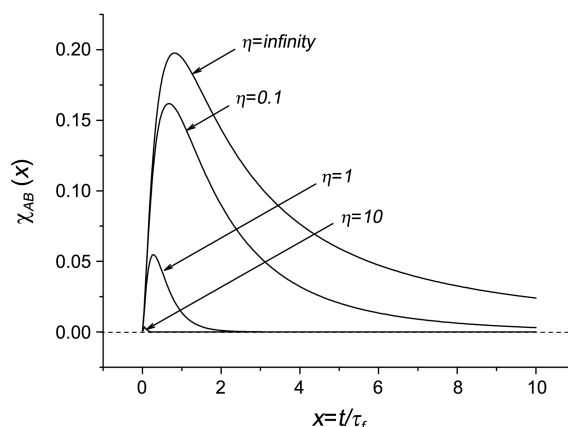


Figure 4. Time behaviour of functions $\chi_{AB}(x)$ (7.14) for different values of $\eta = \tau_f/\tau_A$.

equations for Correlation Patterns read

$$\begin{cases} (\partial_t - \hat{\mathcal{L}}_{AB} - \hat{v}_f + k([A]_i + [B]_i) + 1/\tau_A + 1/\tau_B) \pi_{AB}(\vec{r}, t) \\ = \hat{v}_f[A]_i[B]_i - k([A]_i, \pi_{BB}(\vec{r}, t) + [B]_i, \pi_{AA}(\vec{r}, t)) \\ (\partial_t - \hat{\mathcal{L}}_{AA} + 2k[B]_i + 2/\tau_A) \pi_{AA}(\vec{r}, t) = -2k[A]_i, \pi_{AB}(\vec{r}, t) \\ (\partial_t - \hat{\mathcal{L}}_{BB} + 2k[A]_i + 2/\tau_B) \pi_{BB}(\vec{r}, t) = -2k[B]_i, \pi_{AB}(\vec{r}, t). \end{cases} \quad (7.12)$$

In the general case it is difficult to solve these equations and we restrict ourselves to the particular case of equal lifetimes $\tau_A = \tau_B$. Then the equations differ from Eqs. (5.2) by similar additional terms on l.h.s. and it can be immediately seen that the kernel of integrodifferential MET kinetic equation differs from kernel (5.7) by additional exponential factor $\exp(-\frac{2(t-t_0)}{\tau_A})$ only as for reaction $A + A \rightarrow C$. Thus in a similar way we conclude that the source J_{AB} in the equation of GET

$$\frac{d[A]_i}{dt} = -K(t)[A]_i[B]_i - [A]_i/\tau_A + J_{AB}(t) \quad (7.13)$$

differs from source (6.13) in changing Markovian kinetics $[A]_i^m$ (2.6) by new Markovian kinetics (7.2). Thus for $\phi_{AB}(y) \equiv \chi_{AB}(k[A]_0 t)$ we obtain

$$\begin{aligned} \phi_{AB}(y) = -6\eta^{5/2} e^{-2y} \left\{ g(y) - (1 + \eta e^{-y})^{-4} \left[\frac{1}{4\eta^2 \sqrt{y}} (1 - e^{-y})^2 (1 + 2\eta e^{-y})^2 \right. \right. \\ \left. \left. + (1 + \eta) w(\sqrt{y}) - \frac{1}{\sqrt{2}} w(\sqrt{2}y) \right] \right\} \end{aligned} \quad (7.14)$$

where $y = k[A]_0 \eta t$ and

$$g(y) = \exp(-y) \int_0^{\sqrt{y}} \exp(z^2) (1 + \eta \exp(-y) \exp(z^2)) dz \quad (7.15)$$

Properties of this function are investigated in Appendix. At $\eta \rightarrow 0$ we obtain the previous result (6.14) as it should be. At long times using asymptote $g(y)$ at $y \rightarrow \infty$

$$g(y) \cong \frac{1}{4\eta(1+\eta)^2 \sqrt{y}} \left\{ \frac{(1+2\eta)}{\eta} + \frac{1}{2y} \left(1 + \eta \ln \frac{1+\eta}{\eta} \right) \right\} \quad (7.16)$$

we have

$$\chi_{AB}(k[A]_0 t) \cong - \frac{3 \left\{ 2(1+\eta)^2 \eta \ln \frac{1+\eta}{\eta} + 2 + \eta - 2\eta^2 \right\}}{8(1+\eta)^4 (k[A]_0 t)^{3/2}} \exp(-2k[A]_0 t). \quad (7.17)$$

We see that as in the reaction $A + A \rightarrow C$ apart from the exponential decay (due to finite lifetime of reactants) the additional power law decay (due to encounters) takes place. However in contrast to the reaction $A + A \rightarrow C$ in the reaction $A + B \rightarrow C$ power laws are the same for stable and nonstable reactants. Really at $\eta = 0$ Eq. (7.14) reproduces the same power law $\frac{3}{4} (k[A]_0 t)^{-3/2}$ as follows Eq. (6.14) at large times. The time behavior of $\chi_{AB}(k[A]_0 t)$ is shown in Figure 4.

At $\eta \geq 1$ and $k[A]_0 t \cong 1$ the inhomogeneous terms responsible for the accumulation of macroscopic correlations become exponentially small. At $k[A]_0 t \ll 1$, when the exponential decay is negligible, the inhomogeneous terms are also small, since macroscopic correlations are not accumulated during that short times. Thus in this case, the accumulation of macroscopic correlations should be neglected at all, and the Encounter Theory based on the concept of independent encounters may be used.

Summary

Based on the non-Markovian kinetic equations derived in the literature using the currently existing many-particle method for the derivation of non-Markovian binary kinetic equations, we have analyzed the Encounter Theory (ET) notions for the widely occurring diffusion assisted irreversible bulk reactions $A + A \rightarrow C$ and $A + B \rightarrow C$ in dilute solutions for arbitrary ratio of initial concentrations of reactants.

The Encounter Theory which is the analog of the Collision Theory in gases considers the reactants in solution as a gas placed in chemically inert continual medium. According to these concepts, the reactants are for the most time in the

process of free random walks, and the reaction takes place on their encounters (the analog of collisions) the characteristic duration of which is essentially less than the mean time between them. Under such conditions, the encounters (as well as collisions in gases) were traditionally treated as independent (i.e., the effects of the encounters occurring at different instants of time are uncorrelated, and therefore additive).

As in gases, these concepts lead to differential kinetic equations (rate equations) differing from formal chemical kinetics equations based on the kinetic law of mass action just in the time dependence of the rate constant at the initial stage of the reaction. Note that the familiar Waite superposition decoupling yields the rate equations (Smoluchowski type equation) corresponding to the Encounter Theory concepts of the independence of pair encounters of reactants in solution.

However, in contrast to collisions, the encounter consists of a series of re-contacts among which there can be contacts of reactants separated by essential distances (spatial meso-scale). In this case if the reaction causes the change in the mean time of free walks due to reactant concentration variation in the course of the reactions $A + A \rightarrow C$ and $A + B \rightarrow C$ (except the case of B reactants in excess), then it is to lead to the relation between the encounter reservoirs and free random walks in the bulk. In other words, the encounters of reactants will be correlated, and this is to affect the form of kinetic equations with allowance for macroscopic correlation accumulation in the reservoir of free walks.

The analysis of the non-Markovian binary kinetic equations of the reactions derived on the basis of many-particle consideration of the reacting systems shows that the agreement with the Encounter Theory takes place when the Integral Encounter Theory (IET) is used which in this method is just a step in the derivation of kinetic equations. It allows solely for two-particle correlations, and fails to consider reactant correlation simultaneously with the encounter partner and reactant in the bulk. Hence it has a restricted time range of validity where the above correlations are insignificant.

However, the next step in the derivation of kinetic equations resulting in the final binary kinetic equation of the Modified Encounter Theory (MET) not only extends the applicability interval of the theory to the entire interval of binary kinetics and, but in full agreement with the above physical arguments, reveals macroscopic correlations induced by the encounters in the reservoir of free walks in the bulk. First these correlations increase with the increasing number of the encounters but then they decay under the action of the encounters in accordance with the familiar assertion concerning correlation decay. This means that the encounters of reactants in solution become correlated on a rather long time interval of the reaction course. It is reasonable to call such a non-Markovian theory (final MET equations written in the Regular form) taking account of dependent pair encounters the non-Markovian Generalized Encounter Theory (GET).

In a particular case of the reaction $A+B \rightarrow C$ with equal mobilities of A and B species (in this case $\bar{D}_{AA} = \bar{D}_{AB} = \bar{D}$)

and equal initial concentrations $[A]_0 = [B]_0$ that are equal to the concentration of A species in the reaction $A + A \rightarrow C$ kinetics in the framework of the Encounter Theory (and formal chemical kinetics) of both reactions $A + A \rightarrow C$ and $A + B \rightarrow C$ (at equal elementary event rates) in the framework of the Encounter Theory (and formal chemical kinetics) are the same. However, the kinetics of both reactions in the context of GET differ due to different manifestations of macroscopic correlations.

In the reaction $A + B \rightarrow C$ accumulation of macroscopic correlations proceeds slower as compared to the reaction $A + A \rightarrow C$ of identical reactants. The reason is that in this reaction conservation of the correlations arising in the reaction pair AB occurs due to their transfer into reactionless pairs AA and BB . Accumulation of macroscopic correlations in the reaction $A + A \rightarrow C$ accelerates the reaction, while in the reaction $A + B \rightarrow C$ it inhibits chemical transformation.

The force interactions between reactants do not change the character of time dependence of additional sources responsible for the macroscopic correlations accumulation and refines the macroscopic steady-state parameters only.

For non-stable reactants, the initial stage of the accumulation of macroscopic correlations does not depend on the lifetimes that is in accordance with the known fact that in irreversible reactions the decay of reactants does not affect the kinetic coefficients. The decay of non-stable reactants manifests itself only on macroscopic time scale (between sequential encounters) leading to additional (to the decay due to the encounters) exponential decay. But for the reaction $A + A \rightarrow C$ of identical particles $A + B \rightarrow C$, in contrast to the reaction $A + B \rightarrow C$, the internal decay changes the power law (responsible for the decay due to the encounters) that becomes slower than for the corresponding reaction of stable species.

In the case where the decay time is less or of the order of time between the encounters, accumulation of correlations may be neglected, and the Encounter Theory (based on the concept on the independence of pair encounters) can be used over the entire range of binary kinetics.

In the general case, the non-Markovian kinetics due to the accumulation of macroscopic correlations manifests itself at fairly long times when reactants decayed deeply in the process of chemical reaction. Thus for practical investigation of chemical kinetics the Encounter Theory may be employed.

However, the existence of the accumulation of the macroscopic correlations is principally important, since it can manifest itself in the experiments where long time tails of the kinetics play a dominant role in the formation of experimentally observed phenomena (for example, Chemically Induced Nuclear Dynamic Polarization (CIDNP) at weak singlet-triplet mixing or the kinetics of multistage reactions, when the long time kinetics of the intermediates play the decisive role in the formation of the products observed).

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Appendix: Investigation of the Function $g(y)$

The function $g(y)$ (7.15) diverges at $\eta \rightarrow 0$. In this case $y \rightarrow 0$, but $x = k[A]_0 t$ can be of a finite value. Let us change the integration variable z to the variable $\tau = \sqrt{\eta}z$ and obtain

$$\eta^{5/2} g(y) = \varphi(x) = \int_0^{\sqrt{x}} \frac{d\tau}{(1+x-\tau^2)^3}. \quad (\text{A1})$$

Calculation of the integral in Eq. (A1) gives the desired expression.

For searching the asymptotic behavior of $g(y)$, let us represent it changing the integration variables in an equivalent form and put $\eta \gg 1$

$$\begin{aligned} g(y) &= \frac{1}{2} \int_0^y \frac{\exp(-z) dz}{\sqrt{y-z}(1+\eta-\exp(-z))^3} \cong \\ &\cong \frac{1}{2\sqrt{y}} \int_0^\infty \left(1 + \frac{z}{2y}\right) \frac{\exp(-z) dz}{(1+\eta-\exp(-z))^3}. \end{aligned} \quad (\text{A2})$$

Calculations of the integrals in r.h.s of Eq. (A2) give the desired expansion (7.16).

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