Apparent Rate Constant for Diffusion-Controlled Threemolecular reaction

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Abstract

We present simple explicit estimates for the apparent reaction rate constant for threemolecular reactions. For small concentrations and $d > 1$, it depends only on the diffusion coefficients and sizes of the particles. For small concentrations and $d \leq 1$, it is also time–dependent. For large concentrations, it gains the dependence on concentrations.
I. INTRODUCTION

Three molecular processes are important for catalysis [1], where two particles, say $A$ and $B$, react in presence of the third substance, “catalytic cite” — $C$. Possible applications to coagulation were also concerned [2].

To our knowledge, the first attempt to obtain a simple theoretical description of the kinetics of the three molecular reaction

\[ A + B + C \xrightarrow{k_t} \text{Product}, \]  

(1)

where $k_t$ is the “chemical” reaction rate constant, which determines the reaction rate per one threeparticle encounter, was made in [3,4], where the heuristic mean-field like analysis of the reaction kinetics for large $C$ — sites was presented. Recently this subject gained more interest [4,2,6,7].

The theory of the bimolecular diffusion-controlled reactions

\[ A + B \xrightarrow{k_b} \text{Product} \]  

(2)

started with the mean-field type approach in $d = 3$ [8]. The most important result of this theory is the fundamental Smoluchowsky reaction rate constant, $k_{Smol}$, which determines the apparent rate constant $k_{app}$ and, therefore, the mean reaction rate

\[ \frac{dC_A}{dt} = -k_{app}C_AC_B, \]  

(3)

where $C_A$ and $C_B$ are the mean concentrations. Frequently $k_{app}$ obeys the “inverse resistance law” [9,10]

\[ \frac{1}{k_{app}} = \frac{1}{k_{transp}} + \frac{1}{k_{chem}}. \]  

(4)

For the reaction (2) in 3d the “transport” constant $k_{transp} = k_{Smol}$ and the “chemical” constant $k_{chem} = k_b$. First attempts to improve the Smoluchowsky theory concerned corrections to $k_{Smol}$ and it took a long time, starting from the early works [11–16], to recognize

\[ 1 \]  

The Product can contain $C$ and/or $A$ or $B$. 

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that fluctuation effects, which determine the long-time asymptotic for the concentration dependencies, can be important. Contrary to it, in threemolecular reactions theory, the most of the recent works are concentrated on the long time behavior (See, however, \cite{4} where the whole time domain was studied by means of a new elegant method) and/or \( d = 1 \) in spite of the fact that complete mean-field like theory is not finished and the analog of \( k_{Smol} \) was not calculated. Particularly, \cite{3,2,1} stress that for the long-time kinetics of the particular type of the reaction \( (1) \), with \( A \equiv B \equiv C \), i.e. for \( A + A + A \xrightarrow{k_t} lA \) with \( l < 3 \), the fluctuation effects are not decisive and that the concentration of \( A \), \( C_A \), for \( d > 1 \) is governed by

\[
C_A \propto 1/\sqrt{t},
\]

and for \( d = 1 \) contains “logarithmic corrections”

\[
C_A \propto \sqrt{(\ln t)/t}.
\]

In our paper we present simple estimates for the Smoluchowsky-like rate constant, \( k_{th} \), which determines for threemolecular reactions the apparent rate constant in the equation

\[
\frac{dC_A(t)}{dt} = -k_{app}\delta_A C_A(t)C_B(t)C_C(t),
\]

where \( \delta_A \) is the number of \( A \) particles, which enter the reaction, minus the number of \( A \) particles which the Product contains, for all \( d \). We show that: (i) For small \( C \) — sites Eq. (7) leads to the dependence Eq. (5) for \( d > 1 \). For \( d = 1 \) we regain the result, Eq (6), since \( k_{th} \) becomes time dependent. We stress that in this case the result is still mean field one, since the fluctuations are not incorporated (see \cite{17} for more detailed analysis of the fluctuation effects on the \( k \) - particle reactions with different types of initial distributions). However, even for \( d > 1 \), \( k_{app} \) is renormalized by the transport processes and, therefore, it is not equal to \( k_t \). (ii) For large \( C \) — sites \( k_{app} \) in the Eq. (2) becomes a function of the mean concentrations and, therefore, Eqs. (2,4) are not valid.

In order to understand the main scaling laws for \( k_{th} \) we consider first the simplified hoping picture with correlations in the reaction zone and without correlations in larger distance. For
important limiting cases we present also the more traditional, diffusion-reaction equation approach. To make clear the ideas we start with the bimolecular reaction (2).

II. BIMOLECULAR REACTIONS

A. Smoluchowsky theory

According to the Smoluchowsky theory, the concentration of $B$ particles in the distance $r$ from the center of the $A$ particle, $C_B(r, t)$, is governed by the diffusion equation

$$\frac{C_B(r, t)}{dt} = D_{AB} \nabla^2 C_B(r, t),$$

(8)

where $D_{AB} = D_A + D_B$, with the boundary conditions

$$\Phi \equiv S_d D_{AB} \nabla C_B(r, t) \mid_{r=R_{AB}} = k_b C_B(R_{AB}, t),$$

(9)

$$C_B(r = \infty, t) = C_B,$$

(10)

where $R_{AB} = R_A + R_B$ and $\Phi$ is a flux of $B$ particles through the $d$-dimensional sphere, $|r| = R_{AB}$, with the surface $S_d$. The reaction rate is equal to the quasi steady state value of $\Phi$ multiplied by $C_A$. For $d = 3$ it leads to the Eq. (4) with $k_{chem} = k_b$ and $k_{transp} = k_{Smol}$.

$$k_{Smol} = \begin{cases} 
4\pi RD_{AB} & \text{for } d = 3 \\
\frac{2\pi D_{AB}}{\ln \frac{R_{AB}^2}{R}} & \text{for } d = 2 \\
\sqrt{D_{AB}/\pi t} & \text{for } d = 1.
\end{cases}$$

(11)

For $t \gg R_{AB}^2/D$ in $d < 3$ and for $k_b \gg k_{Smol}$ for $d \geq 3$, $k_{app} = k_{Smol}$. In $d = 3$, the deviation of $C_B(r, t)$ from the limiting value, $C_B$, decreases proportional to $R_{AB}/|r|$ and, therefore, the size, $L$, of the “reaction zone”, where the distributions of $A$ and $B$ are correlated, is of the order of the reaction radius $R_{AB}$. Contrary to $d = 3$, in $d = 1$ the correlated region grows proportionally to $\sqrt{D_{AB}t}$. The $d = 2$ case is marginal. For smaller dimensions, $d \leq 2$, the diffusion is recurrent, the space exploration is compact [18], which means that the number
of the returns of the diffusing particle to the origin tends to infinity if $t \to \infty$. Therefore, the volume of the reaction zone equals to

$$\Omega \propto L^d,$$

where

$$L \propto R_{AB} \text{ for } d > 2 \text{ and } L \propto \sqrt{D_{AB}t} \text{ for } d \leq 2.$$  

\[ (12) \]

\[ (13) \]

\[ (14) \]

\[ (15) \]



**B. Hoping model**

Let us now consider the simplified picture of the reaction (2), where the correlations for $A$ and $B$ are present only in the reaction zone and the exchange of $A(B)$ particles between the reaction zone and the non disturbed region is a “one step” process with the frequency, $\nu_{A(B)} \propto D_{A(B)}/L^2$, which equals to the minimum eigenvalue for the corresponding diffusion problem. In this section, we also assume that the concentration of the reacting particles is small, so we can consider only pairs $AB$ and neglect the configurations with more particles $B(A)$ in the reaction zone of $A(B)$. Therefore, the reaction rate is proportional to the number of $AB$ pairs, $N_{AB}$, and the balance equation reads

$$\frac{dN_{AB}}{dt} = \nu_{AB} (\Omega V C_A C_B - N_{AB}) - k_b \frac{N_{AB}}{\Omega},$$  

where $V$ is the total volume of the system and $\nu_{AB} = \nu_A + \nu_B$. The first term in the r.h.s. of Eq. (14) is the rate of jumps into the reaction zone, the second term is is the rate of jumps from the reaction zone and the third term is the reaction rate. The quasi steady state solution of Eq. (14) for the reaction rate leads to the result presented by Eq. (3) and Eq. (4) with $k_{chem} = k_b$ and $k_{transp} = \nu_{AB}\Omega$. Taking advantage of the Eqs. (11)–(13), we conclude that

$$\nu_{AB}\Omega = k_{Smol}$$  

with the accuracy of the insignificant numerical multipliers for $d = 1$ and $d \geq 3$, and with the accuracy of $\propto \log(t)$ corrections for $d = 2$.  

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III. THREEMOLECULAR REACTIONS.

A. Probability distributions.

Consider the reaction (1) with $D_C = 0$. In order to take threemolecular correlations into account we write down the master equation for the joint probability, $P(n_A, n_B)$, to obtain $n_A$ particles $A$ and $n_B$ particles $B$ in the reaction zone, near a $C$—site,

$$\frac{dP(n_A, n_B)}{dt} = I_{\text{diff}} + I_{\text{react}}.$$  \hspace{1cm} (16)

The diffusion and reaction terms are equal to

$$I_{\text{diff}} = -(\nu_A n_A + \nu_B n_B + \nu_A \Omega C_A + \nu_B \Omega C_B) P(n_A, n_B) +$$

$$(n_A + 1)\nu_A P(n_A + 1, n_B) + (n_B + 1)\nu_B P(n_A, n_B + 1) +$$

$$+ \nu_A \Omega C_A P(n_A - 1, n_B) + \nu_B \Omega C_B P(n_A, n_B - 1),$$  \hspace{1cm} (17)

$$I_{\text{react}} = -R(n_A, n_B)P(n_A, n_B) +$$

$$R(n_A + 1, n_B + 1)P(n_A + 1, n_B + 1),$$  \hspace{1cm} (18)

where $R(n_A, n_B)$ is the reaction rate for the reaction zone with the given numbers of $A$ and $B$. We assume that the local reaction rate is equal to the product of $A$ and $B$ concentrations in the reaction zone,

$$R(n_A, n_B) = k_t \frac{n_A n_B}{\Omega^2}.$$  \hspace{1cm} (19)

B. Hoping model

1. Small A and B concentrations (small $C$ — sites)

For small $A$ and $B$ concentrations, $C_A(C_B)\Omega << 1$, we consider only triples, the particles $C$, which have $A$ and $B$ in the reaction zone, and pairs, the particles $C$ which have $A$ or
in the reaction zone. The mean number of \( C \) particles is \( N_C = C_C V \); of \( CA \) pairs — \( N_{CA} = N_C P\{1,0\} \); and of \( CB \) pairs — \( N_{CB} = N_C P\{0,1\} \). The reaction rate is proportional to the number of the triples, \( N_{CAB} = N_C P\{1,1\} \). From the Eqs. (16)-(19) we obtain

\[
\frac{dN_{CA(B)}}{dt} = \nu_A(\Omega V C_C C_{A(B)} - N_{CA(B)}) - \\
\nu_B(\Omega N_{CA(B)} C_{B(A)} + N_{CAB}),
\]

(20)

\[
\frac{dN_{CBA}}{dt} = \nu_B(\Omega V C_C C_B - N_{CB}) + \\
\nu_A(\Omega V C_C C_A - N_C) - k_t\Omega^{-2}N_{CBA}.
\]

(21)

When \( \nu_A \gg \nu_B\Omega C_B \) and \( \nu_B \gg \nu_A\Omega C_A \), the steady state solution of the Eqs. (20),(21) leads to the Eq. (7) for the reaction rate and to Eq. (4) for \( k_{app} \) with \( k_{chem} = k_t \) and \( k_{transp} = \nu_{AB}\Omega^2 \). Taking advantage of the Eqs. (11)-(13), we conclude that with the accuracy of the logarithmic corrections for \( d = 1 \) the threemolecular analog of the Smoluchowsky constant equals to

\[
k_{th} \propto \nu_{AB}\Omega^2 \propto R^{2d-2}D_{AB}.
\]

(22)

When one of the diffusion coefficients, say \( D_B \), tends to zero, Eqs. (20),(21) lead to

\[
\frac{dC_A}{dt} = -\nu_B\Omega \delta_A C_C C_B \propto -k_{Smol}\delta_A C_C C_B.
\]

(23)

2. Large A or B concentrations (large C — sites)

For \( C_{A(B)}\Omega >> 1 \), the analysis of the Eqs. (16)-(19) for the averaged \( A(B) \) concentrations in the reaction zone, \( C_{A(B)}^{(r)} \equiv \sum_{n_A=0}^{\infty}\sum_{n_B=0}^{\infty} P(n_A, n_B) n_{A(B)} / \Omega \), leads to

\[
\frac{dC_{A(B)}^{(r)}}{dt} = \nu_A(C_A^{(r)} - C_{A(B)}^{(r)}) - k_t\frac{C_A^{(r)} C_B^{(r)}}{\Omega}.
\]

(24)

Note, however, that in this case the reaction on the catalytic surface with the typical time \( \tau_{surf}^{-1} \propto R_{A,B}C_{A,B}^{(2)}(D_A + D_B) \) can become the limiting stage of the reaction.
Note that the reaction term (the last term in the right hand side of the Eq. (24)) in this regime decouples into the product of the concentrations. For the quasi steady state Eq. (24) reduces to an algebraic second order equation for the reaction rate. When \( k_tC_B << \nu_A\Omega \), it leads to the Eq. (7) with

\[
k_{\text{app}} = \frac{\nu_A\Omega k_t}{\nu_A\Omega + k_tC_A}.
\]

When \( k_tC_B >> \nu_A\Omega \) and \( k_tC_A >> \nu_B\Omega \), the steady state Eq. (24) leads to

\[
\frac{dC_A}{dt} = \Omega C_C \min(\nu_AC_A, \nu_BC_B).
\]

C. Diffusion approach

1. Small A and B concentrations (small C sites)

For the small concentration limit we propose the following extension of the Smoluchowsky approach to three-molecular reactions. We place the origin into the center of an immovable particle \( C \) and determine the conditional density of triples, \( C_{AB}(r_A, r_B, t)d^d r_A d^d r_B = N_{CAB}(r_A, r_B, t)/(VC_C) \), where \( N_{CAB}(r_A, r_B, t) \) is the number of triples with \( A \) in the volume element \( d^d r_A \) near the end of the \( d \) dimensional radius - vector \( dr_A \) and \( B \) in the volume element \( d^d r_B \) near the end of the \( d \) dimensional radius - vector \( dr_B \). The analog of Eq. (8) reads

\[
\frac{\partial C_{AB}(r_A, r_B, t)}{\partial t} = \left( D_A \nabla^2_{r_A} + D_B \nabla^2_{r_B} \right) C_{AB}(r_A, r_B, t).
\]

For the spherically symmetric system, i.e. for \( D_A = D_B = D/2 \) and \( C_A = C_B \), Eq. (27) reduces to

\[
\frac{\partial C_{AB}(r, t)}{\partial t} = D r^{1-2d} \frac{\partial}{\partial r} \left( r^{2d-1} \frac{\partial C_{AB}(r, t)}{\partial r} \right)
\]

with the following boundary conditions

\[
\lim_{r \to \infty} C_{AB}(r, t) = C_AC_B,
\]
\[ D_{AB} S_{2d} \frac{\partial C_{AB}(r,t)}{\partial r} \bigg|_{r=R} = k_tC_{AB}(R,t), \quad (30) \]

where \( r = \sqrt{r_A^2 + r_B^2} \). The solution of the Eq. (28) with the boundary conditions (29), (30) leads to the Eq. (22) for \( d > 1 \). For \( d = 1 \),

\[ k_{th} \propto \frac{D_{AB}}{\ln \frac{R}{D_{AB}t}}. \quad (31) \]

2. Large \( A \) and \( B \) concentrations (large \( C \) — sites)

Choosing the origin in the center of the \( C \) particle, we write the following decoupled equations for \( A \) and \( B \) concentrations

\[ \frac{\partial C_{A(B)}(r,t)}{\partial t} = D_{A(B)} \nabla^2 C_{A(B)}(r,t) \quad (32) \]

with the boundary conditions

\[ D_{A(B)} S_d \frac{\partial C_{A(B)}(r,t)}{\partial r} \bigg|_{R_{C_{A(B)}}} = k_tC_A(r,t)C_B(r,t). \quad (33) \]

When \( k_tC_B << 4\pi R_{CA}D_A \), the solution of the Eqs. (32–33) leads to the Eq. (7) for the reaction rate with

\[ k_{app} = \frac{k_{Smol}k_t}{k_{Smol} + k_tC_A}. \quad (34) \]

When \( k_tC_B >> 4\pi R_{CA}D_A \) and \( k_tC_A >> 4\pi R_{CB}D_B \), it leads to unusual result

\[ \frac{dC_A}{dt} = 4\pi C_C \min(C_AR_{CA}DA, C_BR_{CB}DB). \quad (35) \]

**IV. DISCUSSION**

Thus, the hoping and diffusion models lead to the similar results for apparent rate constants — for bimolecular reaction: Eqs. (11) and (15) and for threemolecular reactions: Eqs. (22, 23) and Eqs. (31) — for small \( C \) — sites; and Eqs. (25, 26) and Eq. (34, 35) —
for large \( C \) – sites. The diffusion model provides more precise results for the marginal dimensions: \( d = 2 \) for bimolecular reactions, Eq. (11), and \( d = 1 \) for threemolecular reactions, Eq. (31). On the other hand, the hoping model provides an easier way for the analysis of the correlations structure, Section III A, and for small diffusion coefficient limit, Eq. (23).

In small \( C \) — limit the threemolecular \( ABC \) correlations are important, since the reaction act — annihilation of a triple — changes the concentrations of both \( A \) and \( B \) in the reaction zone from it’s maximum value to zero, i.e. \( \delta(C_A^r) \equiv \delta(C_B^r) \equiv C_{A(B)}^r \). At the same time, since the concentrations are small, the linear boundary condition, Eq. (30), is valid. The reaction occurs, when \( A \) particle joins the \( CB \) pair or when \( B \) particle joins the \( CA \) pair. Therefore, the limiting reaction rate, Eqs. (22, 31), in this case equals to the rate of jumps of the particles \( A(B) \) to the reaction zone of \( CB(A) \) pair, multiplied by the concentration of \( CB(A) \) pairs, which means that \( k_{th} \propto \Omega k_{Smol} \). When \( D_B \to 0 \), the reaction is limited by the transport of \( B \) particles to \( C \) and the reaction rate, Eq. (23), is the same as for the bimolecular reaction \( B + C \to 0 \) with \( k_{app} \approx k_{Smol} \).

For large \( C \) — sites fluctuations of \( A \) and \( B \) concentrations in the reaction zone are much smaller than the mean values and, therefore, the decoupled (but non linear) equations for \( A \) and \( B \) concentrations, Eqs. (24) and (32, 33), are valid. For \( k_t \to 0 \), Eqs. (25, 34) predict non renormalized value, \( k_{app} \approx k_t \); for \( k_t \to \infty \), Eqs. (25, 26, 34, 35) predict the same reaction rate as for diffusion- controlled bimolecular reaction. Note that the reaction “chooses” from \( A \) and \( B \) the reagent with the minimum effective reaction rate. More detailed and rigorous analysis of the correlator structure will be published in our subsequent publication.

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\(^3\) An interesting problem concerns the fluctuation induced kinetics in the system with \( C_A R_{CA} D_A = C_B R_{CB} D_B \).
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