

# PHYSICAL REVIEW E

## STATISTICAL PHYSICS, PLASMAS, FLUIDS, AND RELATED INTERDISCIPLINARY TOPICS

THIRD SERIES, VOLUME 51, NUMBER 3 PART B

MARCH 1995

### ARTICLES

#### Apparent rate constant for diffusion-controlled three-molecule reactions

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(Received 28 July 1994)

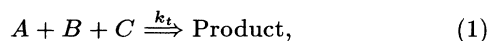
We present simple explicit estimates for the apparent reaction rate constant for three-molecule reactions. For diluted systems and  $d > 1$ , it depends only on the diffusion coefficients and sizes of the reacting particles. For small concentrations and  $d \leq 1$ , it is also time dependent. For concentrated systems, it gains the dependence on concentrations.

PACS number(s): 82.20.-w, 05.20.Dd, 82.40.-g, 05.40.+j

#### I. INTRODUCTION

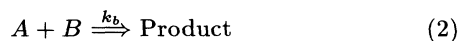
Three-molecule chemical reactions are important for catalysis [1], where two particles, say  $A$  and  $B$ , react in the presence of a third substance, “catalytic site”  $C$ . Applications to coagulation were addressed in [2].

To our knowledge, the first attempt to develop a theoretical description of the kinetics of the three-molecule reaction [3]



was made in [4,5], in which the heuristic mean-field-like analysis of the reaction kinetics for large  $C$  sites was presented. Here  $k_t$  is the “chemical” reaction rate constant, which determines the reaction rate per one three-particle encounter. Recently, three-molecule reactions gained much more interest and important results were obtained [2,6–10].

The theory of the *bimolecular* diffusion-controlled reactions



started with the mean-field-type approach in  $d = 3$  [11].

The most important result of this theory is the fundamental Smoluchowsky reaction rate constant,  $k_{Smol}$ . It determines the apparent rate constant  $k_{app}$  and, hence, the mean reaction rate

$$\frac{dC_A}{dt} = -k_{app}C_A C_B, \quad (3)$$

where  $C_A$  and  $C_B$  are the mean concentrations. Frequently  $k_{app}$  obeys the “inverse resistance law” [12,13]

$$\frac{1}{k_{app}} = \frac{1}{k_{transp}} + \frac{1}{k_{chem}}. \quad (4)$$

For the reaction (2) in 3D the “transport” constant is  $k_{transp} = k_{Smol}$  and the “chemical” constant is  $k_{chem} = k_b$ . For bimolecular reactions in diluted systems the mean-field theory is adequate for a large time domain and therefore first attempts to improve the Smoluchowsky theory concerned concentration-dependent corrections to  $k_{Smol}$ . It took a long time, starting from the early works [14–19], to recognize that fluctuation effects can be significant since they may determine the long-time asymptotic for the concentration dependencies [20].

In the *three-molecule* reactions theory the recent works are concentrated mainly on the long-time behavior and/or  $d = 1$  although a mean-field-like theory is not elaborated on and the analogue of  $k_{Smol}$  is not calculated [21]. Particularly, Refs. [2,7,6] stress that for the long-time kinetics of the reaction (1) with  $A \equiv B \equiv C$ ,

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i.e., for the reaction  $A + A + A \xrightarrow{k_t} lA$  with  $l < 3$ , the fluctuation effects are not decisive and that the concentration of  $A$ ,  $C_A$ , for  $t \rightarrow \infty$  and  $d > 1$  is governed by

$$C_A \propto 1/\sqrt{t}, \quad (5)$$

and for  $d = 1$  contains “logarithmic corrections,”

$$C_A \propto \sqrt{(\ln t)/t}. \quad (6)$$

Corrections such as those that appear in Eq. (6) have been confirmed numerically in [7] and then explained theoretically on the basis of the renormalization group (RG) treatment [9] and heuristic argument [10].

In our paper we present simple explicit estimates for the Smoluchowsky-like rate constant,  $k_{th}$ , which determines for three-molecule reactions in  $d$ -dimensional systems the apparent rate constant in the equation

$$\frac{dC_A(t)}{dt} = -k_{app}\delta_A C_A(t)C_B(t)C_C(t), \quad (7)$$

where  $\delta_A$  = the number of  $A$  particles which enter the reaction *minus* the number of  $A$  particles which the Product contains.

(i) For small  $C$  sites and/or diluted systems we show that for  $d > 1$   $k_{app} = \text{const}$  and for  $d = 1$  it is time dependent. Therefore, Eq. (7) leads to Eq. (5) if  $C_A = C_B = C_C$  and  $t \rightarrow \infty$  in  $d > 1$ . For the same conditions in  $d = 1$  we regain Eq. (6). We stress that in this case the result is still a mean-field result, since the fluctuations are not incorporated (see [22] for a 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 and/or concentrated systems we show that  $k_{app}$  in Eq. (7) becomes a function of the mean concentrations and, therefore, Eqs. (5) and (6) are not valid. For important limiting cases, we present explicit results which are substitutes for Eqs. (5) and (6).

In order to understand the main scaling laws for  $k_{th}$  we consider first a simplified hopping picture with correlations in the reaction zone (RZ) and without correlations at larger distances. For important limiting cases we present also the more traditional diffusion-reaction equation approach. To clarify these ideas we start with the bimolecular reaction (2).

## II. BIMOLECULAR REACTIONS

### A. Smoluchowsky theory

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

$$\frac{\partial C_B(r, t)}{\partial t} = D_{AB} \nabla^2 C_B(r, t), \quad (8)$$

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

$$\Phi \equiv S_d D_{AB} \nabla C_B(r, t) |_{r=R_{AB}} = k_b C_B(R_{AB}, t), \quad (9)$$

$$C_B(r = \infty, t) = C_B, \quad (10)$$

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 Eq. (4) with  $k_{chem} = k$ ,  $k_{transp} = k_{Smol}$ , and

$$k_{Smol} = \begin{cases} 4\pi R D_{AB} & \text{for } d = 3 \\ \frac{2\pi D_{AB}}{\ln \frac{2D_{AB}t}{R^2}} & \text{for } d = 2 \\ \sqrt{4D_{AB}/(\pi t)} & \text{for } d = 1. \end{cases} \quad (11)$$

For  $t \gg R_{AB}^2/D$  in  $d < 3$  and for  $k_b \gg k_{Smol}$  in  $d \geq 3$ ,  $k_{app} = k_{Smol}$ . In  $d = 3$ , the deviation of  $C_B(r, t)$  from the limiting value  $C_B$  decreases as  $R_{AB}/|r|$  and, therefore, the size,  $L$ , of RZ 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. In low dimensions,  $d \leq 2$ , the diffusion is recurrent, the space exploration is compact [23], and hence the number of the returns of the diffusing particle to the origin tends to infinity as  $t \rightarrow \infty$ . Therefore, the volume of RZ [23]

$$\Omega \propto L^d, \quad (12)$$

where

$$L \propto R_{AB} \text{ for } d > 2 \text{ and } L \propto \sqrt{D_{AB}t} \text{ for } d \leq 2. \quad (13)$$

### B. Hopping model

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

$$\frac{dN_{AB}}{dt} = \nu_{AB} (\Omega V C_A C_B - N_{AB}) - k_b \frac{N_{AB}}{\Omega V}, \quad (14)$$

where  $V$  is the total volume of the system and  $\nu_{AB} = \nu_A + \nu_B$ . The first term on the right-hand side of Eq. (14) is the rate of jumps into the RZ, the second term is escape rate from the RZ, and the third term is the reaction rate. The quasi-steady-state solution of Eq. (14) for the reaction rate yields the result, Eq. (3) and Eq. (4) with  $k_{chem} = k_b$  and  $k_{transp} = \nu_{AB}\Omega$ . Taking advantage of

Eqs. (11)–(13) we conclude that

$$\nu_{AB}\Omega = k_{Smol} \quad (15)$$

with the accuracy of the insignificant numerical multipliers for  $d = 1$  and  $d \geq 3$ , and with the accuracy of logarithmic corrections for  $d = 2$ .

### III. THREE-MOLECULE REACTIONS

#### A. Probability distributions

Consider the reaction (1) with an immovable  $C$  site,  $D_C = 0$ . In order to take three-molecule correlations into account we write down the master equation for the joint probability  $P(n_A, n_B)$  of having  $n_A$  particles  $A$  and  $n_B$  particles  $B$  in the RZ, near a  $C$  site,

$$\frac{dP(n_A, n_B)}{dt} = I_{diff} + I_{react}. \quad (16)$$

The diffusion and reaction terms here are given by

$$\begin{aligned} I_{diff} = & -(\nu_A n_A + \nu_B n_B + \nu_A \Omega C_A + \nu_B \Omega C_B)P(n_A, n_B) \\ & + (n_A + 1)\nu_A P(n_A + 1, n_B) \\ & + (n_B + 1)\nu_B P(n_A, n_B + 1) \\ & + \nu_A \Omega C_A P(n_A - 1, n_B) \\ & + \nu_B \Omega C_B P(n_A, n_B - 1), \end{aligned} \quad (17a)$$

$$\begin{aligned} I_{react} = & -R(n_A, n_B)P(n_A, n_B) \\ & + R(n_A + 1, n_B + 1)P(n_A + 1, n_B + 1), \end{aligned} \quad (17b)$$

where  $R(n_A, n_B)$  is the reaction rate for the RZ which contains  $n_A$  particles  $A$  and  $n_B$  particles  $B$ . We assume that the local reaction rate is equal to the product of  $A$  and  $B$  concentrations in the RZ,

$$R(n_A, n_B) = k_t \frac{n_A n_B}{\Omega^2}. \quad (18)$$

#### B. Hopping model

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

For small  $A$  and  $B$  concentrations, such that  $C_A(C_B)\Omega \ll 1$ , we consider only triples, the particles  $C$ , which have  $A$  and  $B$  in the RZ, and pairs, the particles  $C$  which have either  $A$  or  $B$  in the RZ. The mean number of  $C$  particles is  $N_C = C_C V$ ; the mean number of  $CA$  pairs is  $N_{CA} = N_C P\{1, 0\}$ ; and the mean number of  $CB$  pairs is  $N_{CB} = N_C P\{0, 1\}$ . The reaction rate is proportional to the number of the triples,  $N_{CAB} = N_C P\{1, 1\}$ . From Eqs. (16)–(18) we obtain the balance equations

$$\begin{aligned} \frac{dN_{CA(B)}}{dt} = & \nu_A(\Omega V C_C C_{A(B)} - N_{CA(B)}) \\ & - \nu_B(\Omega N_{CA(B)} C_{B(A)} + N_{CAB}), \end{aligned} \quad (19a)$$

$$\begin{aligned} \frac{dN_{CBA}}{d} = & \nu_B(\Omega V C_C C_B - N_{CB}) \\ & + \nu_A(\Omega V C_C C_A - N_{CA}) - k_t \Omega^{-2} N_{CBA}. \end{aligned} \quad (19b)$$

When  $\nu_A \gg \nu_B \Omega C_B$  and  $\nu_B \gg \nu_A \Omega C_A$  (which implies that  $\nu_A \Omega V C_C C_A \gg \nu_B N_{CAB}$  and  $\nu_B \Omega V C_C C_B \gg \nu_A N_{CBA}$ ), the steady-state state solution of Eqs. (19) leads to the Eq. (7) for the reaction rate and to the Eq. (4) for  $k_{app}$  with  $k_{chem} = k_t$  and  $k_{transp} = \nu_{AB}\Omega$ . Taking advantage of Eqs. (11)–(13), we conclude that the three-molecule analogue of the Smoluchowsky constant is equal to [24]

$$k_{th} \propto \nu_{AB}\Omega^2 \propto R^{2d-2} D_{AB} \quad (20)$$

with the accuracy of the logarithmic corrections which appear in 1D.

When one of the diffusion coefficients, say  $D_B$ , becomes small, such that  $D_B/D_A \ll C_A(C_B)\Omega$ , Eqs. (19) lead to

$$\frac{dC_A}{dt} = -\nu_B \Omega \delta_A C_C C_B \propto -k_{Smol} \delta_A C_C C_B, \quad (21)$$

where  $k_{Smol}$  is the Smoluchowsky constant for the reaction  $A + C = 0$ .

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

For  $C_{A(B)}\Omega \gg 1$ , the analysis of Eqs. (16)–(18) for the averaged  $A(B)$  concentrations in the RZ,

$$C_{A(B)}^{(r)} \equiv \sum_{n_A=0}^{\infty} \sum_{n_B=0}^{\infty} P(n_A, n_B) n_{A(B)} / \Omega, \quad (22)$$

leads to

$$\frac{dC_{A(B)}^{(r)}}{dt} = \nu_A(C_{A(B)} - C_{A(B)}^{(r)}) - k_t \frac{C_A^{(r)} C_B^{(r)}}{\Omega}. \quad (23)$$

Note that the reaction term [the last term on the right hand side of Eq. (23)] in this regime *decouples into the product of the concentrations*. For the quasi-steady-state, Eq. (23) reduces to an algebraic second order equation for the reaction rate. When  $k_t C_B \ll \nu_A \Omega$ , it leads to Eq. (7) with

$$k_{app} = \frac{\nu_A \Omega k_t}{\nu_A \Omega + k_t C_A}. \quad (24)$$

When  $k_t C_B \gg \nu_A \Omega$  and  $k_t C_A \gg \nu_B \Omega$ , the steady-state solution of Eq. (23) leads to

$$\frac{dC_A}{dt} = \Omega C_C \min(\nu_A C_A, \nu_B C_B). \quad (25)$$

#### 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-

molecule reactions. We place the origin into the center of an immovable particle  $C$  and determine the conditional density of triples,

$$C_{AB}(r_A, r_B, t) d^d r_A d^d r_B = N_{CAB}(r_A, r_B, t) / (V C_C), \quad (26)$$

where  $N_{CAB}(r_A, r_B, t)$  is the number of triples with a particle  $A$  in the volume element  $d^d r_A$  near the end of the  $d$ -dimensional radius—vector  $dr_A$  and a particle  $B$  in the volume element  $d^d r_B$  near the end of the  $d$ -dimensional radius—vector  $dr_B$ . The analogue of Eq. (8) reads as

$$\frac{\partial C_{AB}(r_A, r_B, t)}{\partial t} = (D_A \nabla_{r_A}^2 + D_B \nabla_{r_B}^2) C_{AB}(r_A, r_B, t). \quad (27)$$

For the “spherically symmetric” system, i.e., for  $D_A = D_B = D$  and  $C_A = C_B$ , Eq. (27) reduces to

$$\frac{\partial C_{AB}(r, t)}{\partial t} = D r^{1-2d} \frac{\partial}{\partial r} \left( r^{2d-1} \frac{\partial C_{AB}(r, t)}{\partial r} \right) \quad (28)$$

with the following boundary conditions:

$$\lim_{r \rightarrow \infty} C_{AB}(r, t) = C_A C_B, \quad (29a)$$

$$S_{2D} \left. \frac{\partial C_{AB}(r, t)}{\partial r} \right|_{r=R} = k_t C_{AB}(R, t), \quad (29b)$$

where  $r = \sqrt{r_A^2 + r_B^2}$  is a distance in 2D dimensional space. The solution of the Eq. (28) with the boundary conditions (29) leads to the Eq. (20) for  $d > 1$ . For  $d = 1$

$$k_{th} \propto \frac{D_{AB}}{\ln \frac{D_{AB} t}{R^2}}. \quad (30)$$

## 2. Large $A$ and $B$ concentrations (large $C$ sites)

We place the origin at the center of  $C$  particle, and write following decoupled equations for  $A$  and  $B$  concentrations

$$\frac{\partial C_{A(B)}(r, t)}{\partial t} = D_{A(B)} \nabla^2 C_{A(B)}(r, t) \quad (31)$$

with the boundary conditions

$$S_d \left. \frac{\partial C_{A(B)}(r, t)}{\partial r} \right|_{|r|=R_{C(A)}} = k_t C_A(r, t) C_B(r, t). \quad (32)$$

The solution of Eqs. (31)–(32) leads to the following expression for the flux through the reaction boundary in the 3D system:

$$\Phi = b - \sqrt{b^2 - 4k_t^2 R_{CA} R_{CB} D_A D_B C_A C_B}, \quad (33a)$$

where

$$b = \frac{2\pi}{2} [4\pi R_{CA} R_{CB} D_A D_B + k_t (C_A R_{CA} D_A + C_B R_{CB} D_B)]. \quad (33b)$$

When  $k_t C_B \ll 4\pi R_{CA} D_A$ , the solution of Eqs. (33) leads to Eq. (7) for the reaction rate. The apparent rate constant is

$$k_{app} = \frac{k_{Smol} k_t}{k_{Smol} + k_t C_A}. \quad (34)$$

When  $k_t C_B \gg 4\pi R_{CA} D_A$  and  $k_t C_A \gg 4\pi R_{CB} D_B$ , it leads to the unusual result

$$\frac{dC_A}{dt} = 4\pi C_C \min(C_A R_{CA} D_A, C_B R_{CB} D_B). \quad (35)$$

## IV. DISCUSSION

Thus the hoping and diffusion models lead to similar results for the apparent rate constants—for the bimolecular reaction: Eqs. (11) and (15), as well as for three-molecule reactions: Eqs. (20), (21), and Eqs. (30), for small  $C$  sites; and Eqs. (24), (25), 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 three-molecular reactions, Eq. (30). On the other hand, the hoping model provides an easier way for the analysis of the correlations structure, see Sec. III A, and for the small diffusion coefficient limit, Eq. (21).

In the small  $C$  limit the three-molecule  $ABC$  correlations are important, since the reaction act—annihilation of a triple—changes the concentrations of both  $A$  and  $B$  in the RZ from its maximum value to zero, i.e.,  $\delta(C_A^r) \equiv \delta(C_B^r) \equiv C_{A(B)}^r$ . Therefore, three-particle correlations cannot be decoupled. Meanwhile, since the concentrations are small, the linear boundary condition, Eq. (29b), is valid. Configurations with more than one particle  $A$  and/or  $B$  in the RZ are improbable and the reaction occurs when the  $A$  particle joins the  $CB$  pair or when the  $B$  particle joins the  $CA$  pair. Therefore, the limiting mean reaction rate, Eqs. (20) and (30), in this case equals to the rate of jumps of the particles  $A(B)$  to the RZ of  $CB(A)$  pair, multiplied by the mean concentration of  $CB(A)$  pairs, which means that  $k_{th} \propto \Omega k_{Smol}$ . When  $D_B \rightarrow 0$ , the reaction is limited by the transport of  $B$  particles to  $C$  and the reaction rate, Eq. (21), is the same as for the bimolecular reaction  $B + C \Rightarrow 0$  with  $k_{app} \Rightarrow k_{Smol}$ .

For large  $C$  sites, fluctuations of  $A$  and  $B$  concentrations in the RZ are much smaller than the mean values and, therefore, the decoupled (but nonlinear) equations for  $A$  and  $B$  concentrations, Eqs. (23), (31), and (32), are valid. For  $k_t \rightarrow 0$ , Eqs. (24) and (34) predict a non-normalized value,  $k_{app} \approx k_t$ ; for  $k_t \rightarrow \infty$ , Eqs. (24), (25), (34), and (35) predict the same reaction rate that one can expect for diffusion-controlled bimolecular reaction. Note that the reaction “chooses” from  $A$  and  $B$  the reagent with the smallest effective reaction rate [25]. More detailed analyses of the correlator structure will be published in a subsequent publication.

## ACKNOWLEDGMENTS

The authors thank A. Blumen, G.S. Oshanin, A.A. Ovchinnikov, and S. Redner for stimulating discussions.

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