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RATES OF DIFFUSION CONTROLLED REACTIONS IN ONE, TWO AND THREE DIMENSIONS

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The dimensionality of diffusion may markedly affect the rate and economy of diffusion controlled reactions. Moreover, the degree of dependence of the steady state rate of these reactions on the concentration of each of the two reacting species is also dictated by the dimensionality and it ranges from linear dependence in the three dimensional case to a nearly square dependence in the one dimensional case. These theoretical observations emerge from a direct analysis of the steady state diffusion controlled rates which are derived here using a simple straightforward approach. This approach is based on the conjecture that in the steady state the rate of diffusional encounters between the two reaction partners equals to the sum of the encounter rates of two independent processes which are obtained by alternately immobilizing one of the reaction partners while the other partner diffuses freely. Unlike Smoluchowski's classical approach, the presented point of view permits to obtain in a unified fashion reaction rates for all dimensionalities.

1. Introduction

Smoluchowski, in his now classical work on diffusion controlled reactions [1], derived the steady state rate of reactions that proceed in solution. For two reacting species A and B that have diffusion coefficients D_A and D_B and that are present in concentrations C_A and C_B, he obtained that the rate at which they react in the diffusion controlled limit equals:

$$\Phi = C_A C_B 4\pi N a(D_A + D_B), \tag{1}$$

where a denotes the encounter radius which is, in this case, the relative separation that the reaction partners have to achieve in order to react, and N is Avogadro's number. To derive eq. (1), Smoluchowski visualized the dynamics of the diffusional encounters in the real solution to be equivalent to that observed in an imaginary system in which one of the reaction partners is immobilized and the other is diffusing freely with an increased diffusion coefficient which is exactly the sum $D_A + D_B$. In this picture the immobilized reactant is acting as a sink to the diffusing one, and the reaction rate is then defined as the steady state flux of diffusing particles into the immobilized particles. The justification for using here the sum of the diffusion coefficients as the diffusion coefficient for the diffusing reactant is based on the observation that, in general, the relative distance between two diffusing particles obeys the same distribution function (in time and space) as do their individual displacements but the former is governed by the sum of the diffusion coefficients. (See also [2].)

Although this observation is true for the case of a pair of diffusing particles, its use as an argument for the above case is not immediately justified since this case involves many uncorrelated diffusing particles and not just a single pair (see comments on this point in [3]). Furthermore, when one attempts to generalize Smoluchowski's analysis to cases where diffusion proceeds in two or in one rather than in three dimensions, one soon encounters severe conceptual difficulties. From such an analysis it turns out, for example, that the reaction rate is crucially dependent on what in the three dimensional case appeared to be an arbitrary choice, namely, which reaction partner is to be immobilized in the imaginary analogue system.

Recently there has been a growing interest in biochemical reactions which are confined to reduced dimensionalities. Accumulating experimental evidence suggests that the rates of various of such biochemical encounter processes are subject to diffusion control. These processes are, for example, the binding between the hormone receptor and the adenylate-cylase in the turkey erythrocyte membrane [4,5], the aggregation phenomena (petch formation) on lymphocyte membranes [6,7] or the guided one dimensional diffusion along a DNA molecule during the process of repressor operator association [8]. The interpretation of such experimental observations requires an extention of Smoluchowski's analysis to cases where the dimensionality of the space in which diffusion proceeds may be lower than three. Therefore, in the following we present an analysis of the steady state rate of diffusion controlled reactions when these reactions proceed either in three dimensions (in solution) or in two dimensions (on/in a membrane) or in one dimension (along a molecule). Due to the fact that our point of view of the process is slightly different than that adopted by Smoluchowski, we can obtain here the steady state rate in a simple manner for any dimensionality. Moreover, we believe that our picture provides an intuitive basis for the understanding of the dynamics of diffusional encounters. It should be mentioned that we deal here with processes which are strictly either one or two or three dimensional and hence we do not examine cases in which diffusion proceeds simultaneously in combined dimensionality, e.g., diffusion in solution + absorption and diffusion on a surface (see [9] and references therein). Also, the transient behavior of these reactions (e.g., [10]) is beyond the scope of this work.

2. Encounter dynamics of diffusing reactants

Imagine now a picture in which particles of type A and B are moving randomly and exerting no long-range forces on each other. If we now make the B particles immobilized and examine the mean time, τ_A, it takes a diffusing A particle to find an immobilized B particle we immediately realize that this time can be considerably different than the mean time, τ_B, it would have taken a diffusing B particle to locate an immoblized A particle. This difference in the mean times originates from the fact that the two encounter partners may have a different diffusion coefficient and hence diffuse the same distance in a different pace. In addition, as we shall explicitly show later, the actual mean net diffusion distance may be different for the above two cases because of differences in concentrations. Our aim in the following is to show that the steady state diffusion controlled rate can be expressed in a general form as:

$$\Phi = C_A/\tau_A + C_B/\tau_B. \qquad (2)$$

Notice the essential basic symmetry of eq. (2) with respect to the behaviour of the two reacting species. This equation, however, yields Smoluchowski result (eq. (1)) for the case of diffusion in three dimensions.

A hint that a symmetric relation of the type given by eq. (2) characterizes a kinetic of diffusional encounters may already be present in the nature of the diffusion process. Since the movements of individual particles are mutually independent, it is reasonable to expect that the process in which two particles accidentally meet can be expressed as the sum of two independent processes – the diffusion of B particles while the A particles are immobilized, and the diffusion of A particles while the B particles are immobilized. To put this explanation in mathematical terms we shall consider now the probability to find a particle in a given point x, where x belongs to the available diffusion space. Let us denote by $P_A(x)$ the unnormalized probability that at a given small time interval, Δt, an A particle is located at a point x, and let us denote by $P_B(x)$ this same probability for a B particle. Notice that here the "point" x is actually a small sphere whose radius is the encounter radius a. Since the movements of the particles are mutually independent at separations greater than the encounter radius, the probability for an encounter between A and B at a point x and a time interval Δt is simply given by the product $P_A(x)P_B(x)$. Consequently, the time derivative of this product averaged over the total space of the system would yield the rate of the reaction at time t. Hence:

$$\Phi = (1/NV) \int_V \{\mathrm{d}[P_A(x)P_B(x)]/\mathrm{d}t\}\mathrm{d}V, \qquad (3)$$

where V is the total diffusion space. Since Φ is given in units of concentration/sec we have divided on the right by Avogadro's number. If we now calculate the time derivative in eq. (3) we obtain:

$$\Phi = (1/NV) \int_V [P_A(x)\, dP_B(x)/dt + P_B(x)\, dP_A(x)/dt]\, dV. \tag{4}$$

In order to calculate the time derivative of the probabilities as is required by eq. (4), we must use additional theoretical observations about the process to the analysis.

Consider the fact that in the absence of a chemical reaction, the probability to find an A or a B particle in a given point is time independent, and consider further that the changes with time of these probabilities are due to encounters between the reactants. Using these considerations it becomes apparent that the rate of change of $P_A(x)$ is equal to the rate at which a B particle reaches the point x and reacts with the A there. Likewise, the rate of change of $P_B(x)$ is equal to the rate at which an A particle reaches x and reacts with the B there. We can easily derive this rate for the case denoted as steady state diffusion. In this case one assumes that the encounter rate between the immobilized and the free particles is such as if the latter has constructed a steady state concentration gradient surrounding the former. For this case we can show that

$$dP_B(x)/dt = 1/\tau_A, \qquad dP_A(x)/dt = 1/\tau_B \tag{5a,b}$$

where, as we have mentioned, τ_A is the mean diffusion time for an A particle to find a B particle when the latter is immobilized at the point x and τ_B is the mean time in the case where B particles search for immobilized A particles. Since the mean diffusion times of eqs. (5) are calculated by assuming that the immobilized reaction partner is uniformly distributed in space (as we shall further discuss in the following), we can now easily integrate eq. (4), taking τ_A and τ_B as constants. Consequently, since from our definition $(1/NV)\int_V P_A(x)dV = C_A$ and $(1/NV)\int_V P_B(x)dV = C_B$, we arrive at eq. (2).

To further clarify the validity of eq. (5), let us recollect the relation between the mean diffusion time and the steady state flux. As it was shown [11], this diffusion time, which describes the behaviour of individual particles and hence is independent of the concentration of these particles, can be extracted from the steady-state diffusion problem. This mean time is equal to the hold-up of the system, divided by the flux in the steady-state. This observation immediately brings us to recognize that eq. (4) and consequently eq. (2), are in fact stating that the steady-state reaction rate is given as the sum of the flux of diffusing A particles into immobilized B particles (the first term of eq. (2)) and the flux of diffusing B particles into immobilized A particles. However, we prefer to look at this reaction rate in terms of mean diffusion times rather than in terms of fluxes, since the latter picture may become conceptually difficult to conceive for cases where concentrations of A and B are substantially different. This is because, in such cases, one would have to consider the flux of very few particles into numerous sinks.

3. Reaction rate calculation

We will now calculate with the help of eq. (2) the diffusion controlled reaction rates in three, two and one dimensions. For this purpose we have to introduce the explicit form of τ_A and τ_B for each case of interest. Since the diffusion problem in hand is in fact the problem of diffusion to small sinks, we can use here the mean diffusion times calculated for this case [12,13].

Consider particles that are released from the boundaries of a closed cell and diffuse freely until they are captured by a sink located at the center of this cell. If we denote by b the radius of the cell and by a the radius of the sink, it can be shown that for cases where $b \gg a$, the mean diffusion times to the sink in the cases of three, two and one dimensional diffusion are [12,13]

$$\text{3D} \quad \tau = b^3/3Da, \tag{6a}$$

$$\text{2D} \quad \tau = (b^2/2D)\ln(b/a), \tag{6b}$$

$$\text{1D} \quad \tau = b^2/2D. \tag{6c}$$

Notice the markedly strong dimensionality dependence of these diffusion times [12]. In cases where the diffusion distance is not much greater than the sink radius a, the mean diffusion time assumes a slightly more complicated form [13]. If we further consider a case where the particles are released not from the boundary of the cell, but rather, that they are released from some arbitrary point in between the wall and the sink, we obtain [13] that in the three and two dimensional cases τ remains practically unmodified, while in the one dimensional case (eq. (6c)) it has to be replaced by $\tau = x_0(2b - x_0)/2D$ where x_0 is the distance between the release point and the sink at the origin.

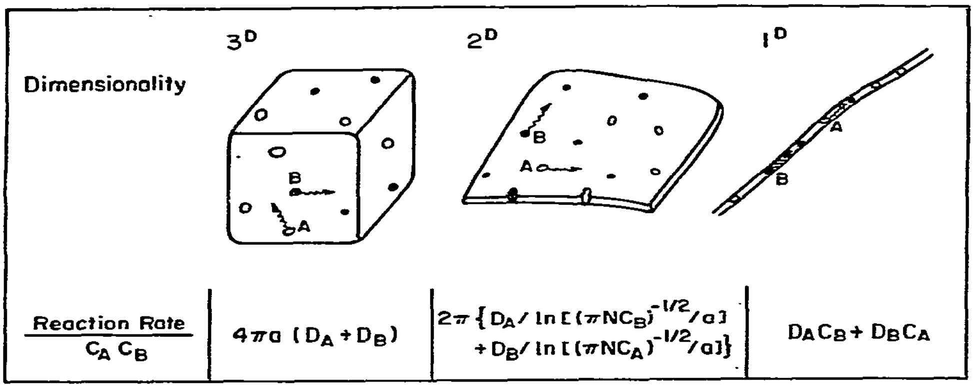

Fig. 1. The steady-state rate of diffusion controlled reaction in three, two and one dimensions. The reaction partners have diffusion coefficients D_A and D_B and are present at average concentrations C_A and C_B. a denotes the separation they have to achieve in order to react and N is Avogadro's number. Notice that the reaction "rate constant" is a true constant only in the case of reaction in three dimensions. In the other two cases it becomes concentration dependent. (To simplify the presentation we have divided the three and the two dimensional rates by N, and the one dimensional rate by $8N^2$.)

If we now return to the derivation of the mean times τ_A and τ_B, we are confronted with the problem to define b of eq. (6). For this purpose we visualize that the array of uniformly distributed immobilized particles (sinks) divides the diffusion space into imaginary cells. The radius of each such a cell is proportional to the concentration of the sinks and there is one sink located at the center of each cell. This "closed cell" approach is based on the observation that if a diffusing particle crosses the cell boundary, it enters into a neighboring cell at a point that is equivalent to the one it left in the first cell (see [14] for a discussion), and hence for our purposes the boundary crossing is unnoticeable.

3.1. Three dimensions

We shall use the above considerations to calculate τ_A and τ_B for the case of three dimensional diffusion. If we designate by b_A and b_B the diffusion distance in cases where B and A, respectively, serve as the sink and further measure the concentration in units of mol/cm^3, we obtain b in cm as

$$(4\pi/3)b_A^3 = 1/NC_B, \qquad (4\pi/3)b_B^3 = 1/NC_A. \qquad \text{(7a,b)}$$

These relations yield for the mean diffusion time of eq. (6a)

$$\tau_A = (4\pi NaC_BD_A)^{-1}, \qquad \tau_B = (4\pi NaC_AD_B)^{-1}. \text{(8a,b)}$$

We can now calculate with the help of these relations and eq. (2) Φ as

$$\Phi = 4\pi NaC_AC_BD_A + 4\pi NaC_AC_BD_B. \qquad (9)$$

Eq. (9) is identical to the Smoluchowski rate given by eq. (1).

3.2. Two dimensions

For the case of two dimensional diffusion we have

$$\pi b_A^2 = 1/NC_B, \qquad \pi b_B^2 = 1/NC_A. \qquad \text{(10a,b)}$$

Notice that in this case the concentrations are measured in units of mol/cm^2. We can now calculate from eq. (6b) the mean diffusion times as

$$\tau_A = (2\pi NC_BD_A)^{-1}\ln[(\pi NC_B)^{-1/2}/a], \qquad \text{(11a)}$$

$$\tau_B = (2\pi NC_AD_B)^{-1}\ln[(\pi NC_A)^{-1/2}/a]. \qquad \text{(11b)}$$

These relations, together with eq. (2), yield for the rate of diffusion controlled reaction in two dimensions

$$\Phi = 2\pi NC_AC_B\,\{D_A/\ln[(\pi NC_B)^{-1/2}/a] + D_B/\ln[(\pi NC_A)^{-1/2}/a]\}. \qquad (12)$$

In cases where the reactants concentration C_A and C_B differ by no more than an order of magnitude the two logarithmic terms in eq. (12) may be assumed equal and with this approximation, eq. (12) can now be simplified to

$$\Phi \approx 2\pi N C_A C_B (D_A + D_B)/\ln[(\pi N C)^{-1/2}/a], \qquad (12a)$$

where C assumes some value between C_A and C_B.

3.3. One dimension

Finally, for the case of one dimensional diffusion in which the concentrations of the reactants are given in mol/cm, we obtain

$$b_A = 1/2NC_B, \qquad b_B = 1/2NC_A. \qquad (13a,b)$$

These relations together with eq. (6c) and (2) yield for the reaction rate

$$\Phi = 8N^2 C_A C_B (D_A C_B + D_B C_A). \qquad (14)$$

For this case, if we assume that the diffusing particles are released at a random location in the cell, we have to substitute eq. (6c) by $\tau = b^2/3D$, and hence will multiply eq. (14) by a factor of 1.5.

As is suggested by eqs. (12) and (14), in two and in one dimensional diffusion, in cases where D_A and D_B are of about the same order of magnitude but the concentration of one of the encounter partners greatly exceeds that of the other partner, then those terms in these equations which contain the diffusion coefficient of the more abundant species are eliminated. Consequently, in such cases the contribution of these abundant particles to the reaction rate is as if they are practically immobilized sinks.

4. Conclusion

The results presented here, which are summarized in fig. 1, support the conjecture that the reduction of dimensionality increases the speed and economy of diffusion controlled reactions, as was originally suggested in [12]. In addition, the concentration dependence of the reaction is altered, and the reaction obtains an increased sensitivity to concentration changes as the dimensionality of diffusion decreases. These points, together with other aspects of the diffusion process as it occurs in living organisms, are discussed in detail elsewhere [13].

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