

16.1: Diffusion to Capture

In this section we will discuss the kinetics of association of a diffusing particle with a target. What is the rate at which a diffusing molecule reaches its target? These diffusion-to-capture problems show up in many contexts. For instance:

1. Molecule diffusing to fixed target(s). Binding of ligands to enzymes or receptors. Binding of transcription factors to DNA. Here the target may have complex topology or target configurations, but it is fixed relative to a diffusing small molecule ($D_{molec} \gg D_{target}$). The diffusion may occur in 1, 2, and/or 3 dimensions, depending on the problem.
2. Bimolecular Diffusive Encounter. Diffusion limited chemical reactions. How do two molecules diffuse into proximity and react? Reaction–diffusion equations.

We will consider two approaches to dealing with these problems:

1. **Steady-state solutions.** The general strategy is to determine the flux of molecules incident on the target from the steady state solution to the diffusion equation with an absorbing boundary condition at the target to account for loss of diffusing molecules once they reach the target. Then the concentration gradient at the target surface can be used to calculate a flux or rate of collisions.
2. **Mean-first passage time.** This is a time-dependent representation of the rate in which you calculate the average time that it takes for a diffusing object to first reach a target.

Diffusion to Capture by Sphere

What is the rate of encounter of a diffusing species with a spherical target? We can find a steady-state solution by determining the steady-state radial concentration profile $C(r)$. Assume that reaction is immediate on encounter at a radius a . This sets the boundary condition, $C(a) = 0$. We also know the bulk concentration $C_0 = C(\infty)$. From our earlier discussion, the steady state solution to this problem is

$$C(r) = C_0 \left(1 - \frac{a}{r} \right)$$

Next, to calculate the rate of collisions with the sphere, we first calculate the flux density of molecules incident on the surface of the sphere ($r = a$):

$$J(a) = -D \frac{\partial C}{\partial r} \bigg|_{r=a} = -\frac{DC_0}{a} \quad (16.1.1)$$

J is expressed as (molec area⁻¹ sec⁻¹) or [(mol/L) area⁻¹ sec⁻¹]. We then calculate the flux, or rate of collisions of molecules with the sphere (molec sec⁻¹), by multiplying the flux density by the surface area of the sphere ($A = 4\pi a^2$):

$$\begin{aligned} j &= \frac{dN}{dt} = JA = \left(\frac{DC_0}{a} \right) (4\pi a^2) \\ &= 4\pi DaC_0 \\ &\equiv kC_0 \end{aligned}$$

We associate the constant or proportionality between rate of collisions and concentration with the pseudo first-order association rate constant, $k = 4\pi Da$, which is proportional to the rate of diffusion to the target and the size of the target.

React-Diffusion

The discussion above describes the rate of collisions of solutes with an absorbing sphere, which are applicable if the absorbing sphere is fixed. For problems involving the encounter between two species that are both diffusing in solution ($A + B \rightarrow X$), you can extend this treatment to the encounter of two types of particles A and B, which are characterized by two bulk concentrations C_A and C_B , two radii R_A and R_B , and two diffusion constants D_A and D_B .

To describe the rate of reaction, we need to calculate the total rate of collisions between A and B molecules. Rather than describing the diffusion of both A and B molecules, it is simpler to fix the frame of reference on B and recognize that we want to describe the diffusion of A with respect to B. In that case, the effective diffusion constant is

$$D = D_a + D_b$$

Furthermore, we expand our encounter radius to the sum of the radii of the two spheres ($R_{AB} = r_A + r_B$). The flux density of A molecules incident on a single B at an encounter radius of R_{AB} is given by eq. (1)

$$J_{a \rightarrow b} = \frac{DC_A}{R_{AB}}$$

Here J describes the number of molecules of A incident per unit area at a radius R_{AB} from B molecules per unit time, [molec A] [area of B] $^{-1}$ sec $^{-1}$. If we treat the motion of B to be uncorrelated with A, then the total rate of collisions between A and B can be obtained from the product of $J_{A \rightarrow B}$ with the area of a sphere of radius R_{AB} and the total concentration of B:

$$\begin{aligned} \frac{dN_{A \leftrightarrow B}}{dt} &= J_{A \rightarrow B} A_{AB} C_B \\ &= J_{A \rightarrow B} (4\pi R_{AB}^2) C_B \\ &= 4\pi D R_{AB} C_A C_B \end{aligned}$$

The same result is obtained if we begin with the flux density of B incident on A, $J_{B \rightarrow A}$, using the same encounter radius and diffusion constant. Now comparing this with expected second order rate law for a bimolecular reaction

$$\frac{dN_{A \leftrightarrow B}}{dt} = k_a C_A C_B$$

we see

$$k_a = 4\pi(D_A + D_B)R_{AB}$$

k_a is the rate constant for a diffusion limited reaction (association). It has units of cm 3 s $^{-1}$, which can be converted to (L mol $^{-1}$ s $^{-1}$) by multiplying by Avagadro's number.

Reactive patches

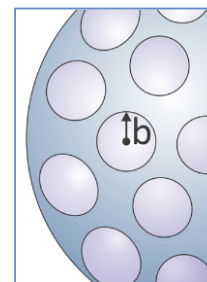
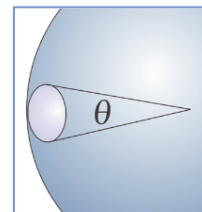
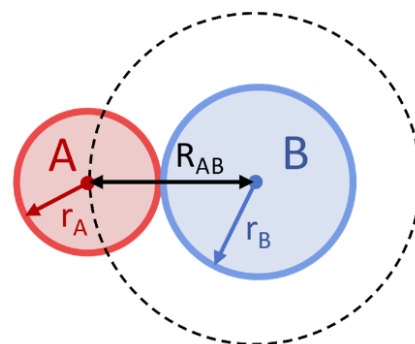
If you modify these expressions so that only part of the sphere is reactive, then similar results ensue, in which one recovers the same diffusion limited association rate ($k_{a,0}$) multiplied by an additional factor that depends on the geometry of the surface area that is active: $k_a = k_{a,0} \cdot [\text{constant}]$. For instance if we consider a small circular patch on a sphere that subtends a half angle θ , the geometric factor should scale as $\sin\theta$. For small θ , $\sin\theta \approx \theta$. If you have small patches on two spheres, which must diffusively encounter each other, the slowing of the association rate relative to the case with the fully accessible spherical surface area is

$$k_a/k_{a,0} = \theta_A \theta_B (\theta_A + \theta_B) / 8$$

For the association rate of molecules with a sphere of radius R covered with n absorbing spots of radius b:

$$k_a = k_{a,0} = \left(1 + \frac{\pi R}{nb}\right)^{-1}$$

Additional configurations are explored in Berg.



1. D. F. Calef and J. M. Deutch, Diffusion-controlled reactions, Annu. Rev. Phys. Chem. 34 (1), 493-524 (1983).

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