

21.5: Diffusion-Limited Reactions

Association Rate

The diffusion-limited association rate is typically approximated from the expression for the relative diffusion of A and B with an effective diffusion constant $D = D_A + D_B$ to within a critical encounter radius $R_0 = R_A + R_B$, as described earlier.

$$k_a = 4\pi R_0 f(D_A + D_B) \quad (21.5.1)$$

One can approximate association rates between two diffusing partners using the Stokes–Einstein expression: $D_A = k_B T / 6\pi\eta R_A$. For two identical spheres (i.e., dimerization) in water at $T = 300$ K, where $\eta \sim 1$ cP = $100 \text{ kg m}^{-1} \text{ s}^{-1}$,

$$k_a = \frac{8k_B T}{3\eta} = 6.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \quad (21.5.2)$$

Note that this model predicts that the association rate is not dependent on the size or mass of the object.

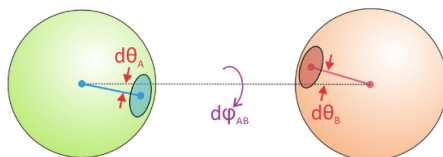
For bimolecular reactions, the diffusion may also include those orientational factors that bring two binding sites into proximity. Several studies have investigated these geometric effects.

Example: Spheres with small binding patches

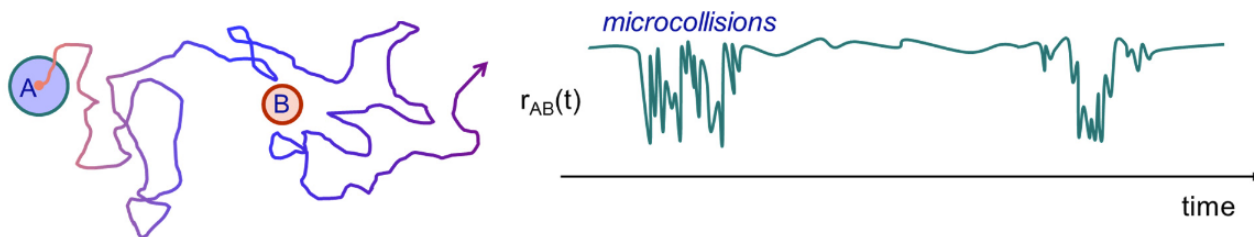
The combined probability that two binding patches are correctly oriented in both reference frames and that both are rotated into the correct azimuthal angle is:

$$P_r = \frac{1}{2}(1 - \cos \delta\theta_A) \frac{1}{2}(1 - \cos \delta\theta_B) \frac{\delta\phi_{AB}}{\pi}$$

$$\approx \frac{1}{16\pi} \delta\theta_A^2 \delta\theta_B^2 \delta\phi_{AB}$$



During diffusive encounter in dilute solution, once two partners collide but do not react, there is a high probability of re-colliding with the same partner before diffusing over a longer range to a new partner. Depending on concentration and the presence of interaction potentials, there may be 5–50 microcollisions with the same partner before encountering a new partner.



Diffusion-Limited Dissociation Rate

For the limit where associations are weak, k_1 and k_{-1} are fast and in equilibrium, and the dissociation is diffusion limited. Then we can calculate k_{-1}



Now we consider boundary conditions for flux moving away from a sphere such that

$$C_B(\infty) = 0$$

$$C_B(R_0) = \left(\frac{4}{3}\pi R_0^3\right)^{-1}$$

The boundary condition for concentration at the surface of the sphere is written so that the number density is one molecule per sphere.

The steady state distribution of B is found to be

$$C_B(r) = \frac{3}{4\pi R_0^2 r} \quad (21.5.4)$$

The dissociation flux at the surface is

$$J = -D_B \left(\frac{\partial C_B}{\partial r} \right)_{r=R_0} = \frac{3D_B}{4\pi R_0^4} \quad (21.5.5)$$

and the dissociation frequency is

$$\frac{J}{4\pi R_0^2} = \frac{3D_B}{R_0^2} \quad (21.5.6)$$

When we also consider the dissociative flux for the other partner in the association reaction,

$$k_{-1} = k_d = 3(D_A + D_B)R_0^{-2} \quad (21.5.7)$$

Written in a more general way for a system that may have an interaction potential

$$k_d = \frac{4\pi D e^{U(R_0)/kT}}{\frac{4}{3}\pi R_0^3 \int_{R_0}^{\infty} e^{U(r)/kT} r^{-2} dr} = 3DR^* R_0^{-3} \quad (21.5.8)$$

Note that equilibrium constants do not depend on D for diffusion-limited association/dissociation

$$K_D = \frac{k_D}{k_A} = \frac{3DR_0^{-2}}{4\pi R_0 D} = \frac{3}{4\pi R_0^3} \quad (21.5.9)$$

Note this is the inverse of the volume of a sphere.

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1. D. Shoup, G. Lipari and A. Szabo, Diffusion-controlled bimolecular reaction rates. The effect of rotational diffusion and orientation constraints, *Biophys. J.* 36 (3), 697-714 (1981); D. Shoup and A. Szabo, Role of diffusion in ligand binding to macromolecules and cell-bound receptors, *Biophys. J.* 40 (1), 33-39 (1982).

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