when it reaches the positive position x_a, corresponding to energy $\Delta U_{a1} = U_a - U_1 = \frac{1}{2}\kappa_1(x_a - x_1)^2$, it has a probability ε_1 of changing into state 2 (Figure A5.1A). This is similar to the problem considered in Figure 4.7. Because the molecule spends about half its time in the negative side of the well, the mean time to escape in the positive direction will be twice the Kramers time t_K (Equation 4.17). The rate constant for the transition between state 1 and state 2 is therefore

$$k_1 = \varepsilon_1 \frac{1}{2t_0} = \varepsilon_1 \frac{1}{\tau_1}\frac{1}{\sqrt{\pi}}\sqrt{\frac{\Delta U_{a1}}{kT}}\exp\left(-\frac{\Delta U_{a1}}{kT}\right)$$

A similar expression holds for k_{-1}. The efficiency factors ε_1 and $\varepsilon_{-1} = 1 - \varepsilon_1$ can be calculated using the equilibrium condition $k_1/k_{-1} = P_2/P_1$. After a little bit of algebra, ε_1 is

$$\varepsilon_1 = \frac{\sqrt{\kappa_2\Delta U_{a2}}}{\sqrt{\kappa_1\Delta U_{a1}} + \sqrt{\kappa_2\Delta U_{a2}}} = \frac{\kappa_2\Delta x_2}{\kappa_1\Delta x_1 + \kappa_2\Delta x_2} \qquad \Delta x_1 = x_1 - x_a \quad \Delta x_2 = x_2 - x_a$$

The ratio of the efficiency factors is the reciprocal of the ratio of the slopes at the transition state.

5.3 Diffusion-Limited Association Rate Constants

Diffusion-Limited Collision Rate Constant

In two or more dimensions, Fick's law is

$$J = -D\nabla c$$

and the diffusion equation is

$$\frac{\partial c}{\partial t} = D\nabla^2 c$$

If there is spherical symmetry, these equations reduce to

$$J(r) = -D\frac{\partial c}{\partial r} \quad \text{and} \quad \frac{\partial c}{\partial t} = D\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right)$$

The steady-state solution ($dc/dt=0$) that satisfies the boundary conditions $c(R) = 0$ and $c(\infty) = c_\infty$ is

$$c(r) = c_\infty\left(1 - \frac{R}{r}\right)$$

This corresponds to an absorbing sphere of radius R in a solution of particles whose concentration a long way from the sphere is c_∞. The total flux of particles through the surface of the sphere is

$$I = \int_{surface} J(R)\cdot da = 4\pi DR c_\infty$$

position x_a, corresponding to energy $\Delta U_{a1} = U_a -$ ...bability ϵ_1 of changing into state 2 (Figure A5.1A). ...n considered in Figure 4.7. Because the molecule ...n the negative side of the well, the mean time to ...tion will be twice the Kramers time t_K (Equation ...the transition between state 1 and state 2 is there-

$$= \epsilon_1\frac{1}{\tau_1}\frac{1}{\sqrt{\pi}}\sqrt{\frac{\Delta U_{a1}}{kT}}\exp\left(-\frac{\Delta U_{a1}}{kT}\right)$$

for k_{-1}. The efficiency factors ϵ_1 and $\epsilon_{-1} = 1 - \epsilon_1$ can ...ilibrium condition $k_1/k_{-1} = P_2/P_1$. After a little bit

$$= \frac{\kappa_2\Delta x_2}{\kappa_1\Delta x_1 + \kappa_2\Delta x_2}\qquad \Delta x_1 = x_1 - x_a \quad \Delta x_2 = x_2 - x_a$$

...actors is the reciprocal of the ratio of the slopes at

Association Rate Constants

on Rate Constant

...s, Fick's law is

$$J = -D\nabla c$$

...is

$$\frac{\partial c}{\partial t} = D\nabla^2 c$$

...etry, these equations reduce to

$$-D\frac{\partial c}{\partial r} \text{ and } \frac{\partial c}{\partial t} = D\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right)$$

...($dc/dt=0$) that satisfies the boundary conditions

$$c(r) = c_\infty\left(1 - \frac{R}{r}\right)$$

...sorbing sphere of radius R in a solution of particles ...g way from the sphere is c_∞. The total flux of parti- ...f the sphere is

$$I = \int_{surface} J(R)\cdot da = 4\pi DRc_\infty$$

Suppose that the particles have radius R_1, that the absorbing sphere (the target) has radius R_2, and that adsorption takes place when the spheres touch. The effective radius is then $R_1 + R_2$. Suppose also that both spheres can freely diffuse, so that the total diffusion coefficient is $D_1 + D_2$. The collision rate constant is

$$k_1 = 4\pi(D_1 + D_2)(R_1 + R_2) = \tfrac{2}{3}\frac{kT}{\eta}\frac{(R_1 + R_2)^2}{R_1 R_2}$$

where we have used the Einstein relation and Stokes' law (see Equation 4.12). The unit is (particles/m³)⁻¹·s⁻¹ and to convert it to the usual $M^{-1}\cdot s^{-1}$ we need to multiply by 1000N (the number of molecules in 1 m³ when the concentration is 1 M). In the case of two identical spheres, the **diffusion-limited on-rate** is 8×10^9 $M^{-1}\cdot s^{-1}$. If one of the spheres is larger than the other, the on-rate will be even larger. On the other hand, if one of the spheres, the target, is thought of as a stationary point ($D_2 = 0$, $R_2 = 0$), then the diffusion limited on-rate is 2×10^9 $M^{-1}\cdot s^{-1}$.

Effect of Orientation on Collision Rates

To calculate the effect of orientation on collision rates, we adopt a different method for calculating the on-rate (Doi, 1975; Bell, 1978). In this method, the on-rate is calculated as the product of the probability of finding the molecule in a particular volume and in a particular range of orientations, and the rate at which the molecule diffuses out of that particular volume and orientation.

The method works well in the absence of orientation constraints. For example, consider a sphere with a stationary point target. The probability that the target is within the sphere is $(4\pi/3)R^3$. The time to diffuse away is $R^2/6D$. The on-rate calculated by this method is

$$k_1 = \frac{4\pi R^3}{3}\frac{6D}{R^2} = \frac{4\pi R}{3}6D = \frac{6kT}{6\pi\eta R} = \frac{4kT}{3\eta}$$

which differs from the exact solution by only a factor of 2.

Now we consider the effect of orientation on the on-rate. Suppose that there is a limited target radius s (~1 Å) and a limited orientation $\theta \sim s/R$. Now the probability is $(4\pi/3)s^3 \times \theta^2/4\pi \times \theta/2\pi = s^6/6\pi R^3$, where the individual terms correspond to the spatial coordinates, the direction of an axis, and the rotation about that axis. The rate of leaving is the sum of the rates for lateral diffusion $(s^2/6D_{lat})^{-1}$ and rotational diffusion $(\theta^2/6D_{rot})^{-1}$. The leaving rate is therefore

$$k_{-1} = \frac{1}{t_{lat}} + \frac{1}{t_{rot}} = \frac{kT}{\eta}\left(\frac{6}{s^2}\frac{1}{6\pi R} + \frac{6}{\theta^2}\frac{1}{8\pi R}\right) = \frac{kT}{\eta}\left(\frac{1}{\pi s^2 R} + \frac{3}{4\pi s^2 R}\right) = \frac{7}{4\pi}\frac{kT}{\eta s^2 R}$$

where the rotational diffusion coefficient for a sphere (D_{rot}) is from Table 6.2. The on-rate is then

$$k_{on} = \frac{s^6}{6\pi R^3}\frac{7kT}{4\pi\eta s^2 R} = \frac{7}{24\pi^2}\frac{kT}{\eta}\left(\frac{s}{R}\right)^4 \cong k_1\left(\frac{s}{2.6R}\right)^4$$

where k_1 is the rate in the absence of orientational constraints.