

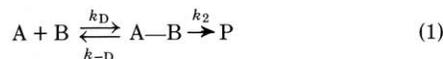
Nearly Encounter-Controlled Reactions

The Equivalence of the Steady-State and Diffusional Viewpoints

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Most kinetics texts discuss the important subject of encounter-controlled rate processes (also called diffusion-controlled rate processes) in liquid-phase solutions (1-7). In such solutions the rates of fast processes are limited by the rate of encounter of pairs of reactants. Slow processes, however, are limited by the rate of passage of the reactant pair over the activation barrier separating it from products. The rate of encounter-controlled reactions may be estimated (1-11) using Smoluchowski's (12) steady-state solution of the diffusion equation. This treatment has been generalized (1-4, 7-9, 11) to treat the more general case than reaction at every encounter by employing the so-called radiation boundary condition, first proposed by Collins and Kimball (13, 14). This allows a unified treatment of fast and slow reactions. Since a pair of reactants undergoing an encounter in the liquid phase remain close much longer than during a typical gas-phase collision, it has sometimes been suggested (6, 8, 10, 15) that the encounter pair can be considered as a transient intermediate, i.e.,



where A and B are solutes, A-B is an encounter pair, and P represents the product or products. In this article the consequences of this suggestion are worked out using the usual method of steady-state concentrations (1, 3, 16-20) (also called the stationary-state hypothesis and the Bodenstein (19) steady-state approximation) and using a notation that allows for comparison to the results obtained from the steady-state diffusion equation with the radiation boundary condition. The results of the two approaches are then shown to be formally identical. This illustrates how the concept of the encounter complex as an unstable intermediate allows a unified treatment of fast and slow reactions. The present comparison of two methods may have useful pedagogical value because the method of steady-state concentrations involves concepts more familiar to many students of chemistry than does the treatment involving the radiation boundary condition applied to the steady-state diffusion equation.

The material in this article is not new, but available textbooks do not present unified discussions of the steady-state and diffusional points of view. The diffusional point of view involves more difficult mathematics whose physical interpretation is not clear to many students of kinetics. Thus, I hope that, by presenting a parallel treatment of the same phenomenon by two approaches, the physical meaning of the important radiation boundary condition in the diffusional derivation will be clarified.

Kinetic Treatment of Encounter Pairs as Intermediates

Consider the two-step mechanism of eqn. (1) where k_D is a bimolecular rate constant for association of encounter pairs, and k_{-D} and k_2 are unimolecular rate constants for their disappearance. The general rate law for this two-step reaction mechanism is not elementary, but it achieves a simple form in various limits. In the limit $k_2 \ll k_{-D}$ the second step becomes rate determining and A-B may be considered to be in equilibrium with A and B.

$$\frac{d[P]}{dt} = k_2[A-B] \quad (2)$$

$$= k_2 K_{A-B}[A][B] \quad (3)$$

$$= \frac{k_2 k_D}{k_{-D}} [A][B] \quad (4)$$

where K_{A-B} is the equilibrium constant for association of encounter pairs. In the other limit, $k_2 \gg k_{-D}$, the first step is rate determining and the rate law becomes

$$\frac{d[P]}{dt} = k_D[A][B] \quad (5)$$

In the intermediate case we may get an approximate rate law by using the method of steady-state concentrations. In this approximation, we assume that the system reaches a steady state in which the concentration of A-B is constant. Thus

$$0 = \frac{d[A-B]}{dt} = k_D[A][B] - (k_{-D} + k_2)[A-B] \quad (6)$$

i.e.,

$$[A-B] = \frac{k_D}{k_{-D} + k_2} [A][B] \quad (7)$$

Then

$$\frac{d[P]}{dt} = k_2[A-B] \quad (8)$$

$$= \frac{k_2 k_D}{k_{-D} + k_2} [A][B] \quad (9)$$

This defines the observed rate constant for the general case as

$$k_{\text{obs}} = \frac{k_2 k_D}{k_{-D} + k_2} \quad (10)$$

Notice that this has the correct limits already stated, i.e.,

$$k_{\text{obs}} \xrightarrow{k_{-D} \gg k_2} \frac{k_2 k_D}{k_{-D}} \quad (11)$$

$$k_{\text{obs}} \xrightarrow{k_2 \gg k_{-D}} k_D \quad (12)$$

in agreement with eqns. (4) and (5), respectively.

Relation of the Steady-State Approximation for the Diffusion Step to Treatment Based on Diffusion Equation

In this section we show that the above treatment of solution reactions, based on the method of steady-state concentrations, is in exact agreement with the treatment based on the diffusion equation. To do this we rederive the usual diffusion equation results (1, 4, 7-9) in order to show how the solutions of this equation should be interpreted in the present context.

The first point we must make is that if a single A and a single B are diffusing in a solvent S, with diffusion coefficients D_{AS} and D_{BS} , their relative motion is the same as for a B dif-

fusing with respect to a fixed A but with diffusion coefficient

$$D_{AB} = D_{AS} + D_{BS} \quad (13)$$

This theorem can be proved by random walk considerations (21) if the particles move independently of each other. This theorem becomes only an approximation for a single A in a bath containing many B (8), but it is often used for this case anyway. We will use this theorem here because it allows us to treat the A + B encounter rate in terms of diffusion of B through a spherical surface at a distance r (to be specified below) from a stationary A. Then the overall rate will be approximated by multiplying the inward flux by the concentration of A.

The equation governing steady diffusion is Fick's first law, which may be written in spherical coordinates for the present problem as ((22), p. 13)

$$J = -D_{AB}A \frac{d[B]}{dr} \quad (14)$$

where J is the number of molecules passing the surface of area A ($= 4\pi r^2$) per unit time in the positive r direction. Then we consider the case where there is a spherically symmetric gradient of B molecules diffusing towards $r = 0$ because the concentration of B molecules is smaller inside the sphere than outside it. This concentration gradient is described in more detail in standard treatments (see (1), p. 497, or (8), p. 135).¹ The concentration gradient around a given A molecule is due to the fact that any B molecules that would be near A in the absence of reaction are likely to have already reacted with it if we are in the steady-state case where reaction is occurring.

Now the reaction rate is to be calculated, as explained in words above, by the relation.

$$-\frac{d[A]}{dt} = [A]J_{in} \quad (15)$$

where J_{in} is the inward flux ($= -J$). The observable bulk reaction rate constant k_{obs} is defined by

$$-\frac{d[A]}{dt} = k_{obs}[A][B]_{\infty} \quad (16)$$

where $[B]_{\infty}$ denotes the bulk value of $[B]$ as opposed to $[B]_r$, the steady-state value of $[B]$ at a distance r from a given A. For a dilute solution, which is assumed here, we may equate $[B]_{\infty}$ to $[B]$ at $r = \infty$, i.e., to the actual concentration in a macroscopic non-depleted region very far from any A molecule. Comparing eqn. (15) to eqn. (16) yields the quantity to be computed

$$k_{obs} = J_{in}/[B]_{\infty} \quad (17)$$

However, if molecules react immediately upon encountering the surface, then $k_{obs} = k_D$. So if we solve for J_{in} with a boundary condition that corresponds to immediate reaction upon encounter of the surface, then

$$k_D = J_{in}^i/[B]_{\infty} \quad (18)$$

where i denotes the immediate reaction boundary condition. Thus we must solve for J_{in}^i in terms of D_{AB} and $[B]_{\infty}$.

First we obtain the general solution of the diffusion equation for $[B]_r$. The general solution of eqn. (14), with $J = -J_{in}$ and $A = 4\pi r^2$, is

$$[B]_r = -\frac{J_{in}}{4\pi r D_{AB}} + b \quad (19)$$

where b is the constant of integration. Clearly we can interpret this constant as

$$b = [B]_{\infty} \quad (20)$$

To go further, i.e., to solve for J_{in} in terms of $[B]_{\infty}$ and D_{AB} , we need to know $[B]_r$ at some boundary $r = \sigma$ or $d[B]/dr$ at $r = \sigma$ or some other additional boundary condition.

First we consider the ir boundary condition. This clearly corresponds to

$$[B]_{\sigma}^{ir} = 0 \quad (21)$$

(This is usually called the Smoluchowski boundary condition.) Substituting eqn. (21) into eqn. (19) gives

$$J_{in}^i = 4\pi\sigma D_{AB}b \quad (22)$$

and using eqn. (20) gives

$$J_{in}^i = 4\pi\sigma D_{AB}[B]_{\infty} \quad (23)$$

Finally, by eqn. (18),

$$k_D = k_{obs}^i = 4\pi\sigma D_{AB} \quad (24)$$

which is a standard result. In applying eqn. (24) one would ordinarily set σ equal to a hard-sphere collision diameter, i.e.,

$$\sigma = r_A + r_B \quad (25)$$

where r_A and r_B are effective encounter radii for A and B.

Next we consider the solution of the diffusion equation for a more general boundary condition than immediate reaction at every encounter. For the general (actual) case, we remove the superscript *ir*, and the steady-state rate is given by eqn. (15)

$$R_{ss} = -\frac{d[A]}{dt} = J_{in}^{ss}[A] \quad (26)$$

However, if $[B]$ could be kept everywhere at its equilibrium value the rate would be

$$R_{eq} = \left(-\frac{d[A]}{dt}\right)_{eq} = k_{eq}[A][B]_{\infty} \quad (27)$$

$$= \frac{[AB]_{eq}}{[AB]_{ss}} R_{ss} \quad (28)$$

$$= \frac{[B]_{\sigma}^{eq}}{[B]_{\sigma}^{ss}} R_{ss} \quad (29)$$

$$= \frac{[B]_{\infty}}{[B]_{\sigma}^{ss}} R_{ss} \quad (30)$$

$$= \frac{[B]_{\infty}}{[B]_{\sigma}^{ss}} J_{in}^{ss}[A] \quad (31)$$

Equating eqn. (27) to eqn. (31) yields

$$[B]_{\sigma}^{ss} = J_{in}^{ss}/k_{eq} \neq 0 \quad (32)$$

This is sometimes called the radiation boundary condition. Substituting eqn. (32) into eqn. (19) gives

$$\frac{J_{in}^{ss}}{k_{eq}} = -\frac{J_{in}^{ss}}{4\pi\sigma D_{AB}} + b \quad (33)$$

Using eqns. (17), (20), and (24) now yields

$$k_{ss} = J_{in}^{ss}/b = (k_D^{-1} + k_{eq}^{-1})^{-1} \quad (34)$$

which is the final result.

For the two-step mechanism considered at the beginning of this article we obtained an explicit expression for k_{eq} , namely, eqn. (4):

$$k_{eq} = k_2 k_D / k_{-D} \quad (35)$$

Substituting this into eqn. (34) yields

$$k_{ss} = k_2 k_D / (k_2 + k_{-D}) \quad (36)$$

¹ A summary: Those A molecules near a B molecule when reaction begins react. Then there is a deficiency of nearby unreacted pairs. Molecules diffuse together to try to achieve an equilibrium spatial distribution, but nearby molecules react so the system achieves a steady-state distribution rather than an equilibrium one.

which is *exactly* the same as the result, eqn. (9), that we derived by the steady-state approximation. Thus the diffusion equation with the radiation boundary condition is both physically and mathematically identical to the steady-state approximation of chemical kinetics.

Summary

A very basic problem in formulating reaction rate expressions for reactions in the solution phase is how to treat the competition between spatial diffusion of reactants to form an encounter complex and the subsequent step of reaction within the encounter complex. The two textbook-level methods for treating this problem are the steady-state approximation and the approximate solution of the appropriate diffusion equation. Usually the problem is treated by one or the other of these methods, and no connection is given. In the present article the equivalence of these methods is demonstrated. It is hoped that this discussion will enable students better to appreciate the physical implications of the mathematics involved in the so-called radiation boundary condition for the diffusion equation.

Acknowledgment

The author is grateful to Warren Reynolds for his comments on some of the material presented here. This work was sup-

ported in part by the National Science Foundation through grant no. CHE80-25232.

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