THE ROLE OF DIFFUSION IN BIMOLECULAR SOLUTION KINETICS

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ABSTRACT An appropriate boundary condition is derived which permits both the bimolecular association and dissociation steps to be simultaneously treated within the framework of the theory of Smoluchowski, Debye, and Collins, and Kimball. Kinetic theory expressions are derived for the intrinsic rate constants. The transient case of the suddenly switched-on reaction is considered as well as the suddenly perturbed equilibrium, but only the time dependence of the rate constants is obtained. The frequency response spectrum for a diffusion-controlled reaction is obtained in the linear approximation and compared with the corresponding Debye relaxation spectrum.

INTRODUCTION

The classical theory of diffusion in bimolecular solution kinetics, as formulated by Smoluchowski (1), Debye (2), Collins and Kimball (3), and Noyes (4), is incomplete because only the association reaction has been considered. Since most rapid reactions are experimentally accessible primarily by relaxation methods (5–8) that involve both association and dissociation processes (7), it is desirable to formulate the complete theory. When this is done a proper interpretation of "diffusion control" of the dissociation reaction emerges for the first time. It is also possible to show from the theory that the concentration gradient disappears for a reaction at equilibrium. This has two consequences:

(a) in any perturbed equilibrium experiment the concentration gradient will be established only *after* the perturbation is applied, so that the effective rate constant is in fact time dependent as it decays to its steady-state value associated with the fully developed concentration gradient; as shown below, the frequency response spectrum for a diffusion-controlled reaction at sufficiently high frequencies may be expected to deviate significantly from the Debye-type spectrum predicted from the steady-state rate constants;

(*b*) any description of the reaction process that divides the initial bimolecular event into a diffusive association step proceeding with a rate characteristic of the concentration gradient around an infinite sink, as calculated by Smoluchowski and

Debye, and a subsequent unimolecular transformation is logically incorrect. The disappearance of the concentration gradient as the reaction nears equilibrium is simply not compatible with the basic premise of such descriptions, which include those presented by Christiansen (9) and Eigen (10). The fact that such descriptions lead to correct formulae for the steady-state rates is not really surprising in view of the fact that simple dimensional analysis, guided only by some notion of the correct limiting forms, also suffices to yield the correct formulae in the steady state. Since there is some likelihood that the concentration gradient may be directly observed in the future by either light or neutron scattering, the correct description of this gradient is not a moot point.

Although the proper distinction between "collisions" and "encounters" of molecules in solution was established long ago by Rabinowitch (11) and Rabinowitch and Wood (11), there still exists no simple kinetic theory description of the collision process in solution. For completeness such a description is offered here.

THE PHYSICAL PICTURE

We consider an infinite volume of solution containing solutes A, B, C which participate in the reaction $A + B \rightleftharpoons C$, and which are initially present at concentrations c_A^0, c_B^0, c_C^0, respectively. We wish to describe the average state of the system as viewed from a typical A molecule. One can obtain a set of pictures of the solution, all at the same time, t, by first placing the origin of the coordinate system on a particular A molecule and plotting the positions of all the other A, B, C molecules, and then repeating the procedure taking the origin on a different A molecule, and so on. If one has obtained such a picture for each of the c_A^0 molecules of A in a unit volume, one may simply superpose all of these pictures so that their origins conicide. The distribution of A, B, C about the common origin in this superposition picture may be used to define the average concentrations about a single A molecule. It is important to note that each A molecule will appear in every picture, as will each B and C molecule, although it will be at the origin of only one. Therefore, the average concentration of any species in the superposition picture is too large by a factor of c_A^0. We assume that any long-range potentials are spherically symmetric. The average concentration of a species (e.g. B) about an A molecule is defined by

$$c_B(r) = \frac{\text{number B molecules in spherical shell } 4\pi r^2 dr}{c_A^0 \, 4\pi r^2 dr},$$

where the spherical shell is taken at distance r from the common origin in the superposition picture. When a particle B reacts with an A, the A-B pair is destroyed and a C is created. That picture centered on the reacted A is dropped from the set of pictures with the consequence that $c_B(r)$ is preferentially decreased at the reaction radius $r = R$. The A-B pair is replaced by a C at the appropriate locations in the remaining pictures. This causes a slight increase in $c_C(r)$ and a slight decrease in

$c_A(r)$, $c_B(r)$ at all r. If the net reaction proceeds toward C so rapidly that almost all of the pictures with a B near the origin are removed from the set, there will appear a substantial void in $c_B(r)$ at small r which gives rise to the well-known concentration gradient. Since the theorem of Smoluchowski applies separately to each relative coordinate $(x^A - x^B)$, $(y^A - y^B)$, $(z^A - z^B)$, and since it applies simultaneously and independently to each A-B pair in the solution, each B particle in the solution will obey the diffusion equation in the appropriate relative coordinates of every single A. Recalling that the superposition picture just contains every B particle in the relative coordinates of every A, it is clear that $c_B(r)$ must also obey the diffusion equation

$$\frac{\partial c_B}{\partial_t}(r, t) = (D_A + D_B)\nabla^2 c_B(r, t) + \nabla \cdot \mathbf{J}_B^f(r, t), \qquad (1)$$

where D_A, D_B are the diffusion coefficients of A, B, and $\mathbf{J}_B^f(r, t)$ is the current density of B particles induced by intermolecular forces. We have ignored the sinks and sources for $c_B(r)$ at $r > R$ arising from the reaction, which is only justified if the total reaction taking place in the time required to reach the steady state is negligible.

The appropriate boundary condition at the reaction radius $r = R$ for a reversible reaction is found from the following considerations. Since one picture with a B at the reaction radius is *removed* from the set for each molecular event A + B → C, and since also one picture with a B at the reaction radius is *adde*d to the set for every molecular event C → A + B, it must be true that the *net* rate of removal $\partial n/\partial t$ of such pictures from the set equals just the net reaction flux Φ (number of forward reactions minus number of reverse reactions in the unit volume per unit time). That is,

$$\frac{\partial n}{\partial t} = \Phi. \qquad (2)$$

Now $\partial r/\partial t$ is just the number of particles B diffusing *inward* across the reaction surface per unit time in the superposition picture. Using Fick's first law about an average A molecule we obtain

$$\frac{\partial n}{\partial t} = + c_A^0 \, 4\pi R^2 D \frac{\partial c_B}{\partial r}(r)\bigg|_{r=R}. \qquad (3)$$

The net reaction flux Φ is readily seen to be

$$\Phi = k_1 c_A^0 c_B(R) - k_2 c_c^0, \qquad (4)$$

where we have employed the notion that it is the average concentration $c_B(R)$ *at the reaction surfaces about the A's* which is important in determining the bimolecular reaction rate. The constants k_1, k_2 are the intrinsic rate constants characterizing the reaction. k_1 is the bimolecular rate constant which applies when the average local (i.e. $r = R$) concentration of one reactant in the vicinity of the other is known. k_2 is the unimolecular rate constant for the spontaneous formation of an A-B pair *at the reaction surface* from a C molecule. Combining Equations 3–5 we obtain our boundary condition

$$\left.\frac{\partial c_{\mathrm{B}}(r)}{\partial r}\right|_{r=R} = \frac{k_1}{4\pi R^2 D}\, c_{\mathrm{B}}(R) - \frac{k_2}{4\pi R^2 D}\,\frac{c_C^0}{c_{\mathrm{A}}^0}\,. \tag{5}$$

Clearly this condition reduces to that of Collins and Kimball in the absence of the reverse reaction (i.e. when $c_C^0 = 0$).

THE STEADY STATE

We follow here the method of Debye (2). In the steady state there will be a constant current density of particles B about an average particle A, thus

$$\mathbf{J}(r) = -D\nabla c_{\mathrm{B}}(r) - \mu c_{\mathrm{B}}(r)\nabla U(r),\ R \leq r \leq \infty, \tag{6}$$

where $U(r)$ is the long-range "potential of average force" discussed by McMillan and Mayer (12), $D = D_{\mathrm{A}} + D_{\mathrm{B}}$, and $\mu = \mu_{\mathrm{A}} + \mu_{\mathrm{B}} = (D_{\mathrm{A}} + D_{\mathrm{B}})/kT$ is the mechanical mobility (i.e. velocity per unit force).

The total current passing inward through a spherical surface S at r is the reaction flux per *unit concentration of A* or $-\mathbf{S}\cdot\mathbf{j} = \phi_M = \Phi/c_A^0$, and Equation 6 becomes

$$\frac{\phi_M}{4\pi R^2 D} = \frac{\partial c_B(r)}{\partial r} + \frac{c_B(r)}{kT}\,\frac{\partial U(r)}{\partial r}\,, \tag{7}$$

which has the general solution (13)

$$c_{\mathrm{B}}(r) = \frac{\phi_M}{4\pi D}\, e^{-\frac{U(r)}{kT}} \int_R^r e^{\frac{U(r')}{kT}}\,\frac{dr'}{r'^2} + \bar{A} e^{-\frac{U(r)}{kT}}\,, \tag{8}$$

where $\bar{A}$ is a constant of integration. The two unknown quantities $\bar{A}$ and ϕ_M are determined by applying the two boundary conditions:

$$c_{\mathrm{B}}(\infty) = c_{\mathrm{B}}^0\,,\ U(\infty) = 0, \tag{a}$$

$$\phi_M = \frac{\Phi}{c_{\mathrm{A}}^0} = \frac{k_1\, c_{\mathrm{A}}^0\, c_{\mathrm{B}}(r) - k_2\, c_{\mathrm{C}}^0}{c_{\mathrm{A}}^0}\,. \tag{b}$$

After some algebra we obtain

$$\Phi = c_{\mathrm{A}}^0\, \Phi_M = \frac{k_1\, 4\pi R D c_{\mathrm{A}}^0\, c_{\mathrm{B}}^0 - k_2\, e^{\frac{U(R)}{kT}}\, 4\pi R D}{k_1\, R \displaystyle\int_R^\infty e^{\frac{U(r)}{kT}}\,\frac{dr}{r^2} + 4\pi R D e^{\frac{U(R)}{kT}}}\,.$$

It is apparent that the effective steady-state forward rate constant is

$$k_f = \frac{k_D\, k_1}{fk_1 + gk_D}, \tag{9}$$

and the effective steady-state reverse rate constant is

$$k_b = \frac{k_D\, k_2\, e^{\frac{U(R)}{kT}}}{fk_1 + gk_D}, \tag{10}$$

where

$$k_D = 4\pi RD = 4\pi(R_{\text{A}} + R_{\text{B}})(D_{\text{A}} + D_{\text{B}}), \tag{11}$$

$$f = R \int_R^{\infty} e^{\frac{U(r)}{kT}} \frac{dr}{r^2}, \tag{12}$$

$$g = e^{\frac{U(R)}{kT}}. \tag{13}$$

When $U(R) \rightarrow 0, f \rightarrow 1, g \rightarrow 1$. We have assumed that the diffusion coefficient is not altered by the long-range intermolecular potential or by proximity of the reaction partners. Noyes and coworkers (14) have presented evidence that such a proximity effect is significant only at very small times and for very large viscosities.

The reaction may be said to be *diffusion limited* when $fk_1 \gg gk_D$, in which case

$$k_f = \frac{k_D}{f}, \quad \text{and} \quad k_b = \frac{k_D k_2}{fk_1} e^{U(R)/kT}. \tag{14}$$

In the *nondiffusion-limited* case, $fk_1 \ll gk_D$, and

$$k_f = \frac{k_1}{g} k_1 e^{-U(R)/kT}, \quad \text{and} \quad k_b = k_2. \tag{15}$$

The reverse reaction rate constant k_b has the property that it is diffusion controlled if, and only if, k_f is diffusion controlled, quite irrespective of the value of k_2. Diffusion control of the reverse reaction comes *only* from the possibility that an A-B pair may be recaptured to form a C before A and B can separate by diffusion. If the outward diffusion process is faster than k_1, the pair will separate and the over-all reverse rate will be just k_2; however, if k_1 is faster than the outward diffusion process, recapture will occur, and an equilibrium concentration of A-B pairs will be established in accord with

$$\frac{c_{\text{A}}{}^0 c_{\text{B}}(R)}{c_{\text{C}}{}^0} = \frac{k_2}{k_1}.$$

The reaction then proceeds as rapidly as particles can diffuse outward from the equilibrium concentration at R, that is

$$\Phi_{\text{out}} = c_{\mathrm{A}}^{0} c_{\mathrm{B}}(R) k_D = c_{\mathrm{C}}^{0} \frac{k_2}{k_1} k_D \tag{16}$$

(in the absence of forces) which accounts for Equation 14. It is easily shown (10) that the solution of Equation 7 in the absence of forces for the case where particles are diffusing out from a spherical surface maintained at concentration $c_{\mathrm{B}}(R)$ into a bulk solution maintained at concentration 0 gives just the outward flux of Equation 16.

It is worthwhile at this point to give kinetic theory formulations for the intrinsic rate constants k_1 and k_2. Considering first the forward reaction, we note that ϕ_M, the rate per unit concentration of A, is given by the average inward current of particles B across the reaction surface:

$$\phi_M = \frac{c_{\mathrm{B}}(R)}{2} 4\pi R^2 p \bar{v}_T, \tag{17}$$

where it has been assumed that one-half of the particles B at R are passing inward at any time, p is the probability that any particular one reacts upon crossing the reaction surface, and $\bar{v}_T$ is the mean thermal relative approach velocity. If it is further assumed that p is independent of the relative approach velocity and that the A's and B's may be characterized by independent Maxwell-Boltzmann distributions, then

$$\bar{v}_T = \frac{m_{\mathrm{A}}^{3/2} m_{\mathrm{B}}^{3/2}}{(2\pi kT)^3} \int_0^\infty \int_0^\infty \int_0^\pi e^{-m_{\mathrm{A}} v_{\mathrm{A}}^2/2kT} e^{-m_{\mathrm{B}} v_{\mathrm{B}}^2/2kT} (v_{\mathrm{A}}^2 + v_{\mathrm{B}}^2 - 2 v_{\mathrm{A}} v_{\mathrm{B}} \cos\theta)^{1/2} \cdot (4\pi) 2\pi \sin\theta \, d\theta v_{\mathrm{A}}^2 \, dv_{\mathrm{A}} v_{\mathrm{B}}^2 \, dv_{\mathrm{B}}, \tag{18}$$

which may be evaluated by standard methods to give

$$\bar{v}_T = 2(2kT/\pi)^{1/2}[(m_{\mathrm{A}} + m_{\mathrm{B}})/m_{\mathrm{A}} m_{\mathrm{B}}]^{1/2},$$

and at last

$$\Phi_{\text{in}} = c_{\mathrm{A}}^{0} c_{\mathrm{B}}(R) \left(8\pi kT \left(\frac{m_{\mathrm{A}} + m_{\mathrm{B}}}{m_{\mathrm{A}} m_{\mathrm{B}}}\right)\right)^{1/2} (R_{\mathrm{A}} + R_{\mathrm{B}})^2 2p, \tag{19}$$

which differs from the usual kinetic theory result by a factor of 2, and also by the substitution of the local concentration $c_{\mathrm{B}}(R)$ in place of the bulk concentration c_{B}^{0}. It is certainly possible that the assumption of *independent* velocity distributions is invalid for nearest neighbors in dense fluids. In this case one may assume that the reactive pair experiences an approximately harmonic potential for mutual displacements from the average nearest neighbor intermolecular separation. Application of the equipartition theorem to the intermolecular coordinate leads to $\bar{v}_T \simeq (kT/2)^{1/2}([m_{\mathrm{A}} + m_{\mathrm{B}}]/[m_{\mathrm{A}} m_{\mathrm{B}}])^{1/2}$, which is close to the independent velocities result.

Thus, in any circumstance the kinetic description is closely approximated by Equation 19.

A kinetic theory description of k_2 is obtained as follows. It is imagined that the reaction surface at $r = R$ may be drawn about the former A molecule even after its combination with a B to form a C. We wish to compute the rate at which B moieties cross the reaction surface outward to become free B molecules. Again it is assumed that the rate is equal to the area times one-half the concentration of B moieties at $r = R$, times the mean relative separation speed of A and B, times the probability p' of escape on a given try. It is reasonable to assume that the mean speed of separation inside the reaction surface just equals the mean speed of approach as in k_1. Then the outward flux ϕ_{out} is

$$\Phi_{\text{out}} = \frac{p'}{2} c_C{}^0 c_B{}'(R) \bar{v}_T 4\pi R^2, \tag{20}$$

where $\bar{v}_T$ is given after Equation 18, and B′ is used to indicate that moiety of C which is related to B. The concentration of B′ at the reaction surface is just $1/(4\pi R^3/3)$ since there is just one B′ moiety per C molecule. Then

$$\phi_{\text{out}} = c_C{}^0 \frac{3}{R} \frac{p'}{2} \bar{v}_T. \tag{21}$$

From equations 19, 21 we obtain

$$k_1 = \left(2\pi kT\left(\frac{m_A + m_B}{m_A m_B}\right)\right)^{1/2} (R_A + R_B)^2 4p, \tag{22}$$

$$k_2 = \left(\frac{2kT}{\pi}\left(\frac{m_A + m_B}{m_A m_B}\right)\right)^{1/2} \frac{3p'}{(R_A + R_B)}. \tag{23}$$

Although Equations 22 and 23 should not be taken too seriously, they do furnish a guide for upper limits to k_1, k_2 (i.e. when $p = p' = 1$), and they also give rise to an appropriate geometrical factor in the equilibrium constant in the absence of specific covalent forces (i.e. when $p = p' = 1$), thus

$$K_c = \frac{c_C}{c_A c_B} = \frac{k_f}{k_b} = \frac{4\pi R^3}{3} e^{-U(R)/kT}. \tag{24}$$

Of course K_c is an equilibrium constant only for concentrations and is, in fact, not a true constant at all since $U(R)$ will always be concentration dependent. However, if the activity coefficients f_A, f_B, f_C are chosen to be unity at infinite dilution, then K_c may be related to the true equilibrium constant K_0 at infinite dilution. Thus,

$$\frac{c_C{}^0}{c_A{}^0 c_B{}^0} = \frac{a_C{}^0}{a_A{}^0 a_B{}^0} = K_0 = 4\pi R^3 e^{-V(R)/kT}, \tag{25}$$

where $V(R)$ is the long-range potential of average force at infinite dilution. From the van't Hoff equation, $K_0 = -RT \ln \Delta F_0$, we have

$$\frac{\Delta F_0}{RT} = \frac{V(R)}{kT} - \ln \frac{4\pi R^3}{3}. \tag{26}$$

Now, at any finite concentration

$$\frac{c_C}{c_A c_B} = \frac{f_A f_B}{f_C} \frac{4\pi R^3}{3} e^{-V(R)/kT}, \tag{27}$$

and from Equation 24 we have

$$U(R) = V(R) - \ln \frac{f_A f_B}{f_C}. \tag{28}$$

Equation 27 is essentially the same as that derived by Fuoss (15) for ion-pair formation using the Debye-Huckel theory. Precise conductance measurements in solvents of varying dielectric constant (16) and in solutions at different temperatures (17) support the validity of an equation of the form of Equation 27. Equation 28 is novel and appears to offer an interesting method for estimating $U(R)$ in concentrated solutions when $V(R)$ and f_A, f_B, f_C are either known or subject to independent estimates. Equation 28 may be obtained directly from Equations 9 and 10 without recourse to the kinetic theory discussion.

Finally it should be noted from Equations 24 and 25 that the equilibrium constant is independent of the viscosity of the solution. Although this conclusion has been long surmised, the treatment here constitutes the first kinetic proof of any rigor.

Below are exhibited the general expressions and limiting cases for two commonly assumed forms of the intermolecular potential:

(*a*) If $U(r) = z_A z_B e^2/\epsilon r$ (Coulomb's law), where z_A, z_B are the valences of A and B, respectively, e is the electronic charge and ϵ the relative dielectric constant, then

$$k_f = \frac{k_1 k_D}{\frac{R\epsilon kT}{z_A z_B e^2}\left(e^{z_A z_B e^2/R\epsilon kT} - 1\right)k_1 + k_D e^{z_A z_B e^2/R\epsilon kT}}, \tag{29}$$

and

$$k_b = \frac{k_2 k_D e^{z_A z_B e^2/R\epsilon kT}}{\frac{R\epsilon kT}{z_A z_B e^2}\left(e^{z_A z_B e^2/R\epsilon kT} - 1\right)k_1 + k_D e^{z_A z_B e^2/R\epsilon kT}}. \tag{30}$$

In the diffusion-controlled limit these become

$$k_f = \frac{k_D z_A z_B e^2}{R\epsilon kT} \frac{1}{\left(e^{z_A z_B e^2/R\epsilon kT} - 1\right)}, \tag{31}$$

which is the result of Debye (2), and

$$k_b = \frac{k_2 k_D z_A z_B e^2}{k_1 R\epsilon kT(1 - e^{-z_A z_B e^2/R\epsilon kT})}. \tag{32}$$

In the nondiffusion-controlled limit

$$k_f = k_1 e^{-z_A z_B e^2/R\epsilon kT} \quad \text{and} \quad k_b = k_2. \tag{33}$$

(*b*) If

$$U(r) = \frac{1}{2}\left\{\frac{e^{\kappa R_A}}{1+\kappa R_A} + \frac{e^{\kappa R_B}}{1+\kappa R_B}\right\} \frac{z_A z_B e^2}{\epsilon kT}\left(\frac{1-\kappa r}{r}\right),$$

where

$$\kappa = \left\{\frac{4\pi e^2}{\epsilon kT} \sum_i n_i z_i^2\right\},$$

then to lowest order of approximation (i.e. $\kappa \rightarrow 0$ so that

$$\frac{1}{2}\left\{\frac{e^{\kappa R_A}}{1+\kappa R_A} + \frac{e^{\kappa R_B}}{1+\kappa R_B}\right\} \rightarrow 1)$$

we find in general

$$k_f = \frac{k_D k_1}{k_1 \frac{R\epsilon kT}{z_A z_B e^2}(e^{z_A z_B e^2/R\epsilon kT} - 1)e^{-z_A z_B e^2 \kappa/\epsilon kT} + k_D e^{z_A z_B e^2(1/R-\kappa)/\epsilon kT}}, \tag{34}$$

$$k_b = \frac{k_D k_2 e^{z_A z_B e^2/R\epsilon kT}}{k_1 \frac{R\epsilon kT}{z_A z_B e^2}(e^{z_A z_B e^2/R\epsilon kT} - 1)e^{-z_A z_B e^2 \kappa/\epsilon kT} + k_D e^{z_A z_B e^2(1/R-\kappa)/\epsilon kT}}. \tag{35}$$

In the diffusion-controlled limit

$$k_f = \frac{k_D z_A z_B e^2}{R\epsilon kT} e^{z_A z_B e^2 \kappa/\epsilon kT}(e^{z_A z_B e^2/R\epsilon kT} - 1)^{-1}, \tag{36}$$

which is the result of Debye (2) and

$$k_b = k_D \frac{k_2}{k_1} \frac{z_A z_B e^2}{R\epsilon kT}(1 - e^{-z_A z_B e^2/R\epsilon kT})^{-1}. \tag{37}$$

In the nondiffusion-controlled limit

$$k_f = k_1 e^{-z_A z_B e^2/\epsilon kT(1/R-\kappa)}, \tag{38}$$

as found by Bronsted (18), Christiansen (19) and Scatchard (20), and

$$k_b = k_2. \tag{39}$$

It is interesting that in the approximation employed, k_1 depends upon κ quite strongly while k_2 does not. The effect of intermolecular forces arising from electric charges may be estimated for single electronic charges on each molecule (A and B). Assuming $T = 300°\text{C}$, $\epsilon = 80$, $R = 3 \times 10^{-8}$ cm, $k = 1.4 \times 10^{-16}$ ergs/degree, $e = 4.8 \times 10^{-10}$ esu, then $e^2/R\epsilon kT \cong -2.3$ and $e^{-2.3} \cong (1/10)$. We ask what are the relative changes in the values of k_f and k_b produced by the *attracting* electric charges. The largest effect occurs in dilute solution where the charges are unscreened. From Equation 29 above it is seen that k_f is *larger* by a factor ranging from about 2.3 in the diffusion controlled case to 10 in the nondiffusion-controlled limit. Similarly from Equation 30 it is seen that k_b is *smaller* by a factor ranging from 0.23 in the diffusion-controlled case to 1.0 in the nondiffusion-controlled case. Furthermore, either increasing the reaction radius R above 3 A or increasing the salt concentration will sharply decrease these effects. It is apparent, then, that unless a number of electronic charges are involved, the forward rate constant k_f will *not* be increased by more than a factor of 10, or somewhat less in the diffusion controlled limit.

TRANSIENT EFFECTS

The problem of a reaction where the intrinsic rates are altered discontinuously is treated here for the specific case of no long-range intermolecular forces. Collins and Kimball (3) treated previously the suddenly switched on *forward* reaction. We will examine here only the relaxation of the rate constants in time, since we are at present unable to treat the complete time decay of the reactant concentrations. We must solve

$$\frac{\partial c_B(r, t)}{\partial t} = D\nabla^2 c_B(r, t); \qquad r \geq R, \tag{40}$$

subject to the following boundary conditions

$$c_B(\infty, t) = c_B^0, \tag{a}$$

$$c_B(r, t = 0) = c_B^i(r), \tag{b}$$

$$\left.\frac{\partial c_B}{\partial r}\right|_{r=R} = \frac{k_1}{4\pi R^2 D} c_B(R, t) - \frac{k_2 c_C^0}{4\pi R^2 D c_A^0}, \tag{c}$$

where $c_B^i(r)$ is the initial distribution of B's about the A's in the superposition picture at the time the intrinsic rates are altered, and the third boundary condition is just Equation 5. We are interested primarily in just two circumstances for the initial concentration: (*a*) $c_B^i(r) = c_B^0$, $r \geq R$, corresponding to uniform concentration, and (*b*) whatever $c_B(r)$ applies when a steady state, including equilibrium, is present at the time the rates are altered. We shall solve first for the uniform case

$$c_B^i(r) = c_B^0. \qquad (b')$$

The solution is effected by Laplace transformation of Equation 40 and the boundary conditions (a), (b'), (c) and is given by

$$\frac{c_B(r, t)}{c_B^0} = 1 - \frac{R - \beta}{r}\left[erfc\left(\frac{r - R}{\sqrt{4Dt}}\right) - e^{Dt/\beta^2}e^{(r-R)/\beta}\cdot erfc\left(\frac{\sqrt{Dt}}{\beta} + \frac{r - R}{\sqrt{4Dt}}\right)\right], \qquad (41)$$

where $1/\beta = 1/R(1 + [k_1/4\pi RD])$, and

$$erfc(x) = \frac{2}{\sqrt{\pi}}\int_x^\infty e^{-x^2}\, dx. \qquad (42)$$

Equations 2 and 3 may be combined to give the total reaction flux as

$$\Phi = c_A^0 4\pi R^2 D \left.\frac{\partial c_B(r, t)}{\partial r}\right|_{r=R}. \qquad (43)$$

Substitution of Equation 41 into Equation 43 gives, after some rearrangement,

$$\Phi = \left\{\frac{k_D k_1 c_A^0 c_B^0 - k_2 k_D c_C^0}{k_1 + k_D}\right\}\left\{1 + \frac{R - \beta}{\beta}e^{Dt/\beta^2} erfc\,\frac{\sqrt{Dt}}{\beta}\right\}, \qquad (44)$$

$$\Phi = k(t)c_A^0 c_B^0 - kc_C^0, \qquad (45)$$

where

$$k_f(t) = \frac{k_1 k_D}{k_1 + k_D}\{1 + F(t)\}, \qquad (46)$$

$$k_b(t) = \frac{k_2 k_D}{k_1 + k_D}\{1 + F(t)\}, \qquad (47)$$

and $F(t) = [[R - \beta]/\beta]e^{Dt/\beta^2} erfc(\sqrt{Dt}/\beta)$ approaches 0 as $t \rightarrow \infty$, giving the usual steady-state result. The important point is that the apparent rate constants $k_f(t)$ and $k_b(t)$ are themselves functions of the time at very small times. Since $(R - \beta)/\beta = k_1/k_D$ the amplitude of the change in the rate constants will only be significant for very rapid (i.e. $k_1 \gg k_D$) intrinsic rates. To provide some idea of the time required to relax the rate constants to their steady-state value we may note that $e^{x^2} erfc(x) = 0.178$ when $x = 3$, which corresponds to $\sqrt{DT}/\beta = 3$ or $t = 9\beta^2/D$. When $k_1 \gg k_D$, then $\beta \cong Rk_D/k_1$. If we assume that $k_1 = 10k_D$, $R = 5$ A, then $k(t = 0) = 10\, k_1 k_D/(k_1 + k_D)$, and $k_f(t)$ will have decayed to about one-third of this value in approximately 10^{-10} sec. This relaxation of the rate constant itself arises from the process of establishing the diffusion gradient.

It is apparent from Equation 41 that in the steady state, $c_B(r)$ is given by

$$c_B(r) = c_B{}^0 - c_B{}^0\left(1 - \frac{k_2{}^0 c_C{}^0}{k_1{}^0 c_A{}^0 c_B{}^0}\right)\frac{R - \beta_0}{r}, \tag{48}$$

where $k_{11}{}^0$, $k_1{}^0$, β_0 are the values which hold in the steady state (which we are going to alter subsequently). If the steady state happens to be the equilibrium state, then it is clear that the concentration gradient vanishes. It is now assumed that the intrinsic rate constants become k_2, k_1 after the perturbation. We must solve Equation 40 subject to the conditions (a), (c), and Equation 48 at $t = 0$. The solution is

$$\Phi = k_f(t)c_A{}^0 c_B{}^0 - k_b(t)c_C{}^0, \tag{49}$$

where

$$k_f(t) = \frac{k_D k_1}{k_D + k_1}\left\{1 + \frac{R - \beta}{\beta}\, e^{Dt/\beta^2} erfc\left(\frac{\sqrt{Dt}}{\beta}\right)\right\}$$
$$\cdot\left[1 - \left(1 - \frac{k_2{}^0 c_C{}^0}{k_1{}^0 c_A{}^0 c_B{}^0}\right)\left(\frac{\dfrac{k_1{}^0}{k_1{}^0 + k_D}}{\dfrac{k_1}{k_1 + k_D}}\right)\right] + \left(1 - \frac{k_2{}^0 c_C{}^0}{k_1{}^0 c_A{}^0 c_B{}^0}\right)\frac{k_1{}^0 k_D}{k_1{}^0 + k_D}, \tag{50}$$

$$k_b(t) = \frac{k_D k_2}{k_D + k_1}\left\{1 + \frac{R - \beta}{\beta}\, e^{Dt/\beta^2} erfc\left(\frac{\sqrt{Dt}}{\beta^2}\right)\right\}. \tag{51}$$

It is apparent from Equation 50 that if the reaction was in equilibrium before the perturbation was turned on, then the terms containing $1 - (k_2{}^0 c_C{}^0/k_1{}^0 c_A{}^0 c_B{}^0)$ vanish, leaving the usual result, which is to be expected since there are no gradients in equilibrium and they must be reestablished from zero after the perturbation is switched on. The existence of gradients in a steady state before the perturbation is switched on affects only the forward rate constant, as might be expected from the interpretation of diffusion control given previously. Again it is to be emphasized that these expressions display only the time dependence of the rate constant at very small times and in no way account for the bulk reactant concentrations in the same time interval. The bulk concentration changes are taken up in the next section where the frequency response spectrum for a diffusion-controlled reaction is derived.

FREQUENCY RESPONSE SPECTRUM FOR A DIFFUSION-CONTROLLED REACTION

If the reactive solution is subject to a periodic perturbation of the pressure or temperature, then the intrinsic rate constants will be given in the linear approximation by

$$\begin{aligned} k_1(t) &= \mathrm{k}_1{}^0 + \Delta k_1 e^{i\omega t}, \\ k_2(t) &= k_2{}^0 + \Delta k_2 e^{i\omega t}, \end{aligned} \tag{52}$$

where ω is the angular frequency of the imposed perturbation and k_1^0, k_2^0 are the values which apply at the equilibrium temperature and pressure. It is assumed that this periodic alteration of the intrinsic rate constants gives rise to periodic changes in the reactant, concentrations. That is.

$$\begin{aligned} c_{\mathrm{A}}(t) &= c_{\mathrm{A}}{}^0 + \overline{\Delta \mathrm{A}}\, e^{i\omega t}, \\ c_{\mathrm{B}}(r, t) &= c_{\mathrm{B}}{}^0 + \Delta \mathrm{B}(r) e^{i\omega t}, \\ c_{\mathrm{C}}(t) &= c_{\mathrm{C}}{}^0 + \overline{\Delta \mathrm{C}}\, e^{i\omega t}, \end{aligned} \tag{53}$$

where $c_{\mathrm{A}}{}^0$, $c_{\mathrm{B}}{}^0$, and $c_{\mathrm{C}}{}^0$ are the equilibrium concentrations (the absence of gradients in equilibrium was established in the preceding section) in the superposition picture. In this problem the diffusion equation in the superposition picture becomes

$$\frac{\partial c_{\mathrm{B}}}{\partial t}(r, t) = D\nabla^2 c_{\mathrm{B}}(r, t) + \left.\frac{\partial c_{\mathrm{B}}}{\partial t}\right|_{\text{source}}, \tag{54}$$

where the source term is needed to account for the periodic production and consumption of B's at large distance from the origin. We have

$$\begin{aligned} \left.\frac{\partial c_{\mathrm{B}}}{\partial t}\right|_{\text{source}} = i\omega \Delta \mathrm{B}(r = \infty) e^{i\omega t} &= i\omega \overline{\Delta \mathrm{A}} e^{i\omega t} \\ &= -i\omega \overline{\Delta \mathrm{C}} e^{i\omega t}, \end{aligned} \tag{55}$$

since $\Delta \mathrm{B}(r = \infty) = \overline{\Delta \mathrm{A}} = -\overline{\Delta \mathrm{C}}$ from the stoichiometry of the reaction. The boundary condition at the reaction surface is obtained by combining the usual expressions for the reaction rate per unit concentration of A's:

$$\begin{aligned} \phi_M = \{ &(k_1{}^0 + \Delta k_1 e^{i\omega t})(c_{\mathrm{A}}{}^0 + \overline{\Delta \mathrm{C}}_{\mathrm{A}}\, e^{i\omega t})(c_{\mathrm{B}}{}^0 + \Delta \mathrm{B}\,(R) e^{i\omega t}) \\ &- (k_2{}^0 + \Delta k_2 e^{i\omega t})(c_{\mathrm{C}}{}^0 + \Delta \mathrm{C}\, e^{i\omega t})\} / (c_{\mathrm{A}}{}^0 + \overline{\Delta C}_{\mathrm{A}} e^{i\omega t}), \end{aligned} \tag{56}$$

and

$$\phi_M = 4\pi R^2 (D_0 + \Delta D e^{i\omega t}) \left.\frac{\partial c_{\mathrm{B}}(r, t)}{\partial r}\right|_{r=R}, \tag{57}$$

where $D(t) = (D + (\Delta D_{\mathrm{A}} + \Delta D_{\mathrm{B}}) e^{i\omega t}$ is the now time-dependent diffusion coefficient. Keeping only terms which are first-order in small quantities and their gradients we obtain

$$\Delta \mathrm{B}(R) = R \frac{k_D}{k_1{}^0} \left.\frac{\partial \Delta \mathrm{B}(r)}{\partial r}\right|_R + \frac{k_2{}^0 \overline{\Delta \mathrm{C}} - k_1{}^0 \overline{\Delta \mathrm{A}} c_{\mathrm{B}}{}^0}{k_1{}^0 c_{\mathrm{A}}{}^0} - \frac{(\Delta k_1 c_{\mathrm{A}}{}^0 c_{\mathrm{B}}{}^0 - \Delta k_2 c_{\mathrm{C}}{}^0)}{k_1{}^0 c_{\mathrm{A}}{}^0}, \tag{58}$$

in which small quantities such as $\Delta \mathrm{A}$ have been neglected in favor of $c_{\mathrm{A}}{}^0$, which is only justified so long as the perturbation is a relatively small one. Finally we note again that

$$\overline{\Delta \mathrm{B}} = \Delta \mathrm{B}(r = \infty) = \overline{\Delta \mathrm{A}} = -\overline{\Delta \mathrm{C}}. \tag{59}$$

To first order in small quantities Equation 54 has the form

$$i\omega \Delta \mathrm{B}(r) = D\nabla^2 \Delta \mathrm{B}(r) + i\omega \overline{\Delta \mathrm{B}}. \tag{60}$$

Equation 60 is now solved subject to Equations 58 and 59. The homogeneous equation obtained from Equation 60 by neglecting the source term is solved in the usual manner to give:

$$\Delta \mathrm{B}(r) = \frac{K e^{-r\sqrt{\frac{\omega}{D}}\left(\frac{1+i}{\sqrt{2}}\right)}}{r}, \tag{61}$$

where K is an undetermined constant. The inhomogeneous Equation 60 can be satisfied by adding a term $\Delta \mathrm{B}(r = \infty) = \overline{\Delta \mathrm{B}}$ to the homogeneous solution Equation 61, and this automatically satisfies Equation 59 as well. The constant K is determined from Equation 58 with the result

$$K = \frac{(Q - \overline{\Delta \mathrm{B}}) e^{\sqrt{\frac{\omega}{D}}\left(\frac{1+i}{\sqrt{2}}\right)^{R}} R}{\left(1 + \frac{R k_D}{k_1{}^0}\sqrt{\frac{\omega}{2D}}\left(\frac{1+i}{\sqrt{2}}\right) + \frac{k_D}{k_1{}^0}\right)}, \tag{62}$$

where

$$Q \equiv \frac{k_2{}^0 \overline{\Delta \mathrm{C}} - k_1{}^0 \overline{\Delta \mathrm{A}} c_{\mathrm{B}}{}^0 - (\Delta k_1 c_{\mathrm{A}}{}^0 c_{\mathrm{B}}{}^0 - \Delta k_2 c_{\mathrm{C}}{}^0)}{k_1{}^0 c_{\mathrm{A}}{}^0}. \tag{63}$$

The instantaneous reaction flux is given by

$$\begin{aligned} \Phi_M &= 4\pi R^2 D e^{i\omega t} \left.\frac{\partial \Delta \mathrm{B}(r)}{\partial r}\right|_R \\ &= \frac{4\pi R^2 D(\overline{\Delta \mathrm{B}} - Q)\left[\sqrt{\frac{\omega}{D}}\left(\frac{1+i}{\sqrt{2}}\right) + \frac{1}{R}\right] e^{i\omega t}}{\left[1 + \frac{R k_D}{k_1{}^0}\sqrt{\frac{\omega}{D}}\left(\frac{1+i}{\sqrt{2}}\right) + \frac{k_D}{k_1{}^0}\right]}. \end{aligned} \tag{64}$$

Recalling that $\Phi = c_{\mathrm{A}}{}^0 \Phi_M$ and setting

$$\Phi = \frac{\partial c}{\partial t}\,\mathrm{C} = i\omega \overline{\Delta \mathrm{C}} e^{i\omega t}, \tag{65}$$

we obtain finally after some algebra our main result, the amplitude of the periodic variation in C:

$$\overline{\Delta C} = \frac{\left(\Delta k_1 c_A{}^0 c_B{}^0 - \Delta k_2 c_C{}^0\right)\left(\dfrac{k_D}{k_D + k_1{}^0}\right)}{\dfrac{1}{\tau_s} + i\omega \dfrac{\left[1 + \left(\dfrac{k_D}{k_D + k_1{}^0}\right) R\sqrt{\dfrac{\omega}{2D}}\,(1+i)\right]}{\left[1 + R\sqrt{\dfrac{\omega}{2D}}\,(1+i)\right]}}, \qquad (66)$$

where

$$\frac{1}{\tau_s} = \frac{k_D}{k_D + k_1{}^0}\,\{k_1{}^0(c_A{}^0 + c_B{}^0) + k_2{}^0\}$$
$$= k_f(c_A{}^0 + c_B{}^0) + k_b$$

and k_f and k_b are the steady-state rate constants derived previously. It is clear that Equation 66 reduces to a normal Debye dispersion for situations where $k_D/(k_D + k_1{}^0) \rightarrow 1$, which is the condition for a nondiffusion-controlled (i.e. $k_D \gg k_1{}^0$) reaction. For a strongly diffusion-controlled reaction $k_D/(k_D + k_1{}^0) \ll 1$, and one does not obtain a Debye type relaxation, unless $R\sqrt{\omega/2D} \ll 1$. In fact, $R\sqrt{\omega/2D}$ will be much less than one until quite high driving frequencies ω are reached. For A, B such that $D \cong 2 \times 10^{-5}$ and $R \cong 4 \times 10^{-8}$ it would require $\omega \sim 2 \times 10^8$ for the deviation from a Debye spectrum to exceed 10%, irrespective of the degree of diffusion control.

It can be seen from Equation 61 that $\Delta B(r)$ varies "sinusoidally' over the region of exponential fall-off. In the steady-state theory no region of exponential fall-off arises. What we have here is a statistical gradient of particles B extending into solution which varies sinusoidally with distance and which is at the same time damped out according to $e^{-r\sqrt{\omega/2D}} = e^{-r/r_0}$, where $r_0 = \sqrt{2D/\omega}$ is the damping distance, and represents the distance diffused by the pair in time $1/\omega$. The ratio R/r_0 of the reaction radius to the damping distance gives the relative extension of the "sinusoidal" gradient into the surrounding solution. For $R/r_0 \ll 1$, the damping distance is large compared to the reaction radius; since the sinusoidal variation also has spatial extent r/r_0, a large damping coefficient r_0 means that one oscillation extends far out into the solution. In this limit the particle concentration will have essentially a simple, undamped $1/r$ or "normal" steady-state dependence for a considerable distance into the solution before damping and sinusoidal behavior are superimposed. Thus, a large r_0 minimizes the effect of the exponential factor, especially at small distances, so that a normal gradient is periodically established and removed in time. Thus, a very slow perturbation will succeed in establishing the concentration gradient adiabatically. If, however the frequency is high, the oscillations in the chemical process occur so rapidly that the normal steady-state gradient cannot be established. In this event the damping constant r_0 is very small and there will be energy dissipation associated with the establishment of the diffusion gradient, which will be reflected in the sound absorption spectrum. The characteristic time for this building the diffusion gradient is $\tau_c = 1/\omega_0 = R^2/2D$, and is about 0.5×10^{-10} sec. Unfortunately, this diffusion relaxation is coupled to the chemical relaxation in such a way that the volume change (which is proportional to $\overline{\Delta C}$) is negligible at such high frequencies unless also $\tau_s \approx 10^{-10}$ sec, which is an exceptionally short chemical relaxation time. Thus, the principal experimental manifestation of the diffusion relaxation will be seen at lower frequencies. It is worthwhile to examine the relaxation spectrum for a particular case. We consider the strongly diffusion-controlled case where $k_1^0 \gg k_D$. The acoustical attenuation coefficient α is proportional to $\omega \cdot Im\Delta C$, and we have in this case

$$\frac{\alpha}{\omega^2} \propto \frac{1/(1 + \sqrt{\omega}\, R/\sqrt{2D})}{1 + \left(\dfrac{\omega\tau_s + \sqrt{\omega}\, R/\sqrt{2D}}{1 + \sqrt{\omega}\, R/\sqrt{2D}}\right)^2}. \tag{67}$$

In Fig. 1 this spectrum is compared with the corresponding Debye spectrum obtained by setting $R = 0$ in Equation 67. For this graph the following parameters were chosen: $R_A = R_B = 2.0 \times 10^{-8}$ cm, $k_1 = 6.0 \times 10^{10}\ \text{M}^{-1}\ \text{sec}^{-1}$, $k_2 = 6.0 \times 10^8\ \text{sec}^{-1}$, $T = 300°K$, $\eta = 0.008$ poise. An initial concentration $c_C{}^i = 0.5$ M of C's is added, and the equilibrium concentration $c_A{}^0$ is calculated from

$$c_A{}^0 = \frac{-1/K + \left((1/K)^2 + \dfrac{4c_C{}^i}{K}\right)^{1/2}}{2} = 0.066\ \text{M},$$

since $K = k_1/k_2 = 100\ \text{M}^{-1}$. Other calculated quantities are $D_A = D_B = 1.37 \times 10^{-5}\ \text{cm}^2\ \text{sec}^{-1}$, $k_D = 8.3 \times 10^9\ \text{M}^{-1}\ \text{sec}^{-1}$, $k_f = 7.3 \times 10^9\ \text{M}^{-1}\ \text{sec}^{-1}$, $k_f = 7.3 \times 10^7\ \text{sec}^{-1}$, and $\tau_s = 0.97 \times 10^{-9}$ sec. It will be noted that the maximum deviation from a Debye spectrum

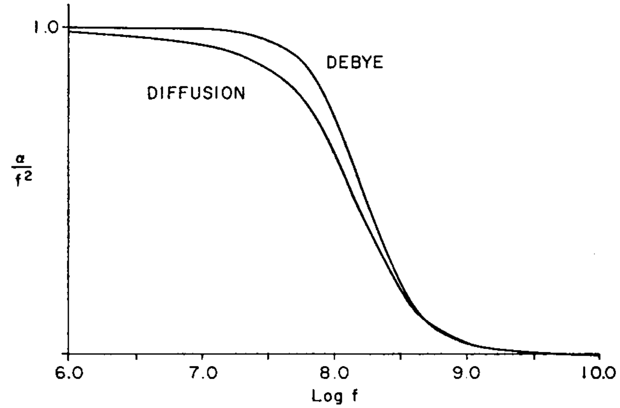

FIGURE 1 Comparison of normalized Debye relaxation spectrum with that obtained from Equation 67. $k_f = 7.3 \times 10^9\ \text{M}^{-1}\ \text{sec}^{-1}$, $k_f = 7.3 \times 10^7\ \text{sec}^{-1}$, $R = 4.0 \times 10^{-8}$ cm, $D = 2.74 \times 10^{-5}\ \text{cm}^2\ \text{sec}^{-1}$, and $\tau_s = 0.97 \times 10^{-9}$ sec. The curve from Equation 67 bears the label "Diffusion."

is about 12–16% and occurs above the midpoint of the relaxation. This diffusional relaxation should, thus, be subject to experimental test with sufficiently precise data in the presently accessible range. When τ is even shorter, as will be found for higher initial concentrations and smaller equilibrium constants, the difference between the two curves becomes much more pronounced. However, the midpoints of such curves lie above the present commonly accussible frequency range which extends only up to 200 Mc. Finally it must be noted that when long-range intermolecular forces are present, the results may be quite different.

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