Diffusion Controlled Effective Reaction Rate for a Surface Reaction with Orientational Selectivity

Siegfried Hess

Institut für Theoretische Physik, Universität Erlangen-Nürnberg, Erlangen

Z. Naturforsch. **33a**, 1243–1250 (1978); received July 26, 1978

The influence of the orientational selectivity of a chemical reaction on the diffusion controlled effective reaction rate is investigated theoretically for the following situation: Nonspherical molecules with random orientation are put into a chemically inert solution at a plane which is a certain distance away from the parallel reaction plane. The reaction frequency at the surface shall depend on the orientation of the figure axis of a molecule relative to the normal of the reaction plane. With a special choice for the orientational dependence of the surface reaction, a continued fraction expansion is derived for the diffusion controlled effective reaction rate. This quantity is discussed and displayed graphically as function of the relevant parameters.

The probability of reaction at a single encounter of two molecules, in general, depends on their mutual orientation. The resulting orientational selectivity of the reaction frequency is of great importance in chemical reactions which are of biological relevance [1]. Many of these processes occur in solutions where the effective reaction rate is controlled by diffusion [2]. In this paper, the influence of the orientational selectivity of the elementary reaction frequency on the diffusion controlled effective reaction rate is studied for the case where one of the reaction partners is a (plane) surface. The other reactants are nonspherical molecules (put into the solution with random orientation) which diffuse towards the reaction surface. The surface reaction frequency shall depend on the orientation of the molecules with respect to the reaction surface. With a special choice for this orientational dependence, an exact expression can be obtained for the effective reaction rate coefficient.

The effect of a chemical asymmetry on the diffusion controlled reaction rate has first been discussed by Solc and Stockmayer [3] for the case where both reaction partners undergo a diffusive motion.

For a theoretical investigation of the somewhat related problem where spherical particles diffuse towards a sphere where only part of the surface is reactive see [4].

This article proceeds as follows. In Part I, some general remarks are made, firstly, on the kinetic equation which governs the orientational distribution function of the diffusing molecules, secondly, on the formulation of the boundary condition at the reaction surface and, thirdly, on the definition of the effective reaction rate. Part II of this paper is devoted to the calculation of the effective reaction rate for a relatively simple case. It is supposed that molecules with random orientation are put into the solution at a constant rate and with a prescribed density at a plane which is parallel to the reaction plane and the distance L away from it.

The surface reaction frequency is assumed to be proportional $1+\beta\cos\vartheta$ where ϑ is the angle between the figure axis of a molecule and the normal vector of the reaction plane. The quantity β (with $-1 \leqq \beta \leqq 1$) is a measure for the orientational selectivity of the surface reaction. Furthermore, for simplicity, correlations between the orientation and the diffusion of the molecules are disregarded. Then, expansion of the distribution function in terms of Legendre polynomial P_j depending on $\cos\vartheta$ and use of the moment method leads to uncoupled differential equations for the number density and averages of the P_j. The stationary solutions of these generalized diffusion equations contain unknown coefficients which have to be determined from the reactive boundary conditions. For $\beta \neq 0$, a set of coupled equations is obtained for the unknown coefficients. These equations can be solved for the ratio between the number densities at the reaction and injection surfaces. It is this quantity which is needed for the effective reaction rate k_{eff}. The solution is expressed in terms of an infinite continued fraction expansion with respect to β^2. In Part III, the obtained results is discussed

---

Reprint requests to Prof. Dr. S. Hess, Institut für Theoreretische Physik, Glückstr. 6, D-8520 Erlangen.

Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition “no derivative works”). This is to allow reuse in the area of future scientific usage.

in some detail. Firstly, the case $\beta = 0$ (no orientational selectivity) is considered. The effective reaction rate k_{eff} depends on L/L_0 where L_0 is a characteristic length determined by the diffusion coefficient and the surface reaction rate. Secondly, and this is the main point of this paper, the case $\beta \neq 0$ is studied. In this case, the effective reaction rate depends also on the ratio l_1/L_0 where l_1 is the decay length of a spatially inhomogeneous average of P_1. Some graphs are presented which show the dependence of the difference between the reaction rates for $\beta \neq 0$ and $\beta = 0$ as functions of $L_0 L^{-1}$, $L_0 l_1^{-1}$, and β. The effect of the orientational selectivity of the surface reaction on the effective reaction rate is largest for $L \approx L_0$. The relative differences between k_{eff} for $\beta = 1$ and $\beta = 0$ can be of the order of 10% under suitable conditions.

It should be mentioned that correlations between the diffusing particles which become of importance at higher concentrations, competition between various reaction sites and possible saturation effects have been disregarded. For a discussion of these points e.g. see [5].

I. General Remarks

1. Distribution Function, Kinetic Equation

A dilute solution of (axisymmetric) molecules in an inert solvent fluid is considered. The unit vector parallel to the figure axis of a molecule is denoted by $\boldsymbol{u}$. Let $f = f(t, \boldsymbol{r}, \boldsymbol{u})$ be the time and space dependent orientational distribution function with the normalization

$$\int f(t, \boldsymbol{r}, \boldsymbol{u}) \, \mathrm{d}^2 u = n(t, \boldsymbol{r}) \tag{1}$$

where n is the number density of the molecules. The local average $\langle \Psi \rangle$ of a quantity $\Psi = \Psi(\boldsymbol{u})$ is, as usual, given by

$$n \langle \Psi \rangle = \int \Psi(\boldsymbol{u}) \, f(t, \boldsymbol{r}, \boldsymbol{u}) \, \mathrm{d}^2 u \, . \tag{2}$$

The time evolution of f is assumed to be governed by the kinetic equation

$$\partial f / \partial t - \boldsymbol{\nabla} \cdot \mathbf{D} \cdot \boldsymbol{\nabla} f + \Omega(f) = 0 \tag{3}$$

where $\mathbf{D} = \mathbf{D}(\boldsymbol{u})$ is the diffusion tensor.

The "collision" term $\Omega(f)$ describes the orientational relaxation of f. Conservation of the number of particles in the interior of the solution implies $\int \Omega(f) \, \mathrm{d}^2 u = 0$ and $\Omega(1) = 0$. A specific form for $\Omega(f)$ will be stated later.

In general, the Eq. (3) has to be supplemented by initial and boundary conditions. For a steady state to be considered in the following it suffices to state the boundary conditions.

2. Boundary Conditions for Surface Reactions

Let the solution be bounded by two (closed) surfaces "I" and "II" with normal unit vectors $\boldsymbol{e}_{\text{I}}$ and $\boldsymbol{e}_{\text{II}}$, see Figure 1 a. At surface I, molecules are put into the solution (at a constant rate) with random orientation. The boundary condition at surface I then is

$$f = (1/4\pi) \, n_{\text{I}} \tag{4}$$

where n_{I} is the (constant) number density at this surface.

The molecules diffuse through the fluid. At surface II, the reaction surface, they shall undergo a chemical reaction (with surface molecules) such that they are effectively removed from the system. The appropriate boundary condition at surface II is

$$\begin{aligned} \boldsymbol{e}_{\text{II}} \cdot \boldsymbol{J}(\boldsymbol{r}, \boldsymbol{u}) &\equiv - \boldsymbol{e}_{\text{II}} \cdot \mathbf{D} \cdot \boldsymbol{\nabla} f(\boldsymbol{r}, \boldsymbol{u}) \\ &= \nu \, l_0 \, f(\boldsymbol{r}, \boldsymbol{u}) \, . \end{aligned} \tag{5}$$

Here, $\boldsymbol{J}(\boldsymbol{r}, \boldsymbol{u})$ is the flux density for molecules with an orientation specified by $\boldsymbol{u}$. The normal unit vector $\boldsymbol{e}_{\text{II}}$ is pointing outward from the fluid. The quantities $\nu = \nu(\boldsymbol{u})$ and l_0 are a reaction frequency and a "reaction length", respectively. It is assumed

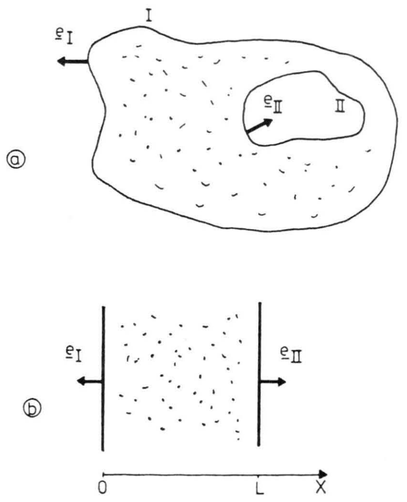

Fig. 1. Schematic diagram of the "experimental set up". The chemically inert solution is confined by the surfaces "I" and "II". The molecules under consideration are put into the solution at surface I and diffuse towards surface II where they undergo a chemical reaction. The outer normals of the surfaces are denoted by $\boldsymbol{e}_{\text{I}}$ and $\boldsymbol{e}_{\text{II}}$.

that ν depends on the angle between $\boldsymbol{u}$ and $\boldsymbol{e}_{\text{II}}$, i.e. surface II acts as a kind of a sieve which selects molecules with a certain orientation. The length l_0 is of the order of the linear dimension of a molecule. The meaning of this quantity is elucidated by the following remarks.

The total number of particles which undergo a chemical reaction per unit time is equal to the total flux I of particles which effectively leave the system "through" surface II, viz.

$$I = \int_{\text{II}} \mathrm{d}\sigma \int \boldsymbol{e}_{\text{II}} \cdot \boldsymbol{J} \, \mathrm{d}^2 u = \int_{\text{II}} \mathrm{d}\sigma \, l_0 \int \nu \, f \, \mathrm{d}^2 u \, . \qquad (6)$$

Here $\int_{\text{II}} \mathrm{d}\sigma$ refers to an integration over surface II. As can be inferred from (6), the ansatz (5) means that molecules in a surface layer of thickness l_0 around surface II react with the frequency ν. Notice, however, that the product νl_0 (reaction velocity) occurs in measurable quantities. Of course, under stationary conditions, the total flux of particles $-\int_{\text{I}} \mathrm{d}\sigma \, \boldsymbol{e}_{\text{I}} \cdot \boldsymbol{J}$ which enter the solution at surface I equals I as given by (6).

3. *Effective Reaction Rate and Reaction Frequency*

As usual, the effective reaction rate coefficient k_{eff} is defined by [2, 3]

$$I = k_{\text{eff}} \, n_{\text{I}} \, . \qquad (7)$$

It is recalled that n_{I} is the number density at the surface where the molecules start rather than their density at the reaction surface. With an effective reaction frequency ν_{eff} defined by

$$\nu_{\text{eff}} \, n_{\text{I}} = \int \nu(\boldsymbol{u}) \, f(\boldsymbol{r}, \boldsymbol{u}) \, \mathrm{d}^2 u \qquad (8)$$

one has

$$k_{\text{eff}} = \int \mathrm{d}\sigma \, l_0 \, \nu_{\text{eff}} \, . \qquad (9)$$

In (8), it is understood that f has to be taken at surface II.

The remainder of this article is devoted to the calculation of the effective reaction frequency and the ensuing effective reaction rate for a simple case.

II. Calculation of the Effective Reaction Rate

1. *Choice of a Simple Special Case*

To focus the attention on the effect of the orientational selectivity of surface reaction on the diffusion controlled effective reaction rate, a simple geometry is considered and the correlation between molecular orientation and the diffusional motion in the interior of the fluid is ignored.

In the following, two parallel planes separated by the distance L are taken as surfaces I and II. The distance of a point from plane I is denoted x, $\boldsymbol{e}_{\text{II}}$ coincides with the unit vector $\boldsymbol{e}^x$ parallel to the x-axis of a coordinate system; the y and z-axes are in plane I; see Figure 1b. It is assumed that the system is homogeneous in the y- and z-directions. This reduces the analysis to an essentially one-dimensional problem and the orientational distribution function f depends on $\boldsymbol{u}$ only through $\cos\vartheta = \boldsymbol{u} \cdot \boldsymbol{e}^x$.

Furthermore, possible correlations between the molecular orientation and their translational motion are ignored, i.e. an isotropic diffusion tensor $\mathbf{D} = D \boldsymbol{\delta}$ is used. The term $\Omega(f)$ of the kinetic equation (3) is specified by

$$\Omega(f) = - w \, \boldsymbol{L} \cdot \boldsymbol{L} \, f \qquad (10)$$

with $\boldsymbol{L} = \boldsymbol{u} \times \partial/\partial \boldsymbol{u}$; $\boldsymbol{L} \cdot \boldsymbol{L}$ is the Laplace operator on a unit sphere. In (10), w is an orientational relaxation frequency often referred to as orientational diffusion coefficient. For a solvent liquid with viscosity η, the hydrodynamical values of the coefficients D and w are given by [6]

$$\begin{aligned} D &= k_{\text{B}} T (6\pi \, \eta \, R_{\text{t}})^{-1} \, , \\ w &= k_{\text{B}} T (8\pi \, \eta \, R_{\text{r}}^3)^{-1} \, , \end{aligned} \qquad (11)$$

where R_{t} and R_{r} are effective radii of a diffusing solute molecule which depend on the molecular shape. The subscripts "t" and "r" refer to the "translational" and "rotational" motions associated with the diffusion in real space and in the orientational space.

2. *Diffusion-Relaxation Equations, Steady State*

For the special geometry under consideration, the distribution function f can be expanded in terms of Legendre polynomials P_j depending on $\cos\vartheta = \boldsymbol{u} \cdot \boldsymbol{e}^x$, viz.

$$f = \frac{1}{4\pi} \left(n + \sum_{j=1}^{\infty} (2j+1) \, n_j \, P_j \right) . \qquad (12)$$

The number density n and the expansion coefficients

$$n_j = n \langle P_j \rangle \, , \quad j = 1, 2, \ldots, \qquad (13)$$

are functions of t and x. Insertion of (12) into Eq. (3) with an isotropic diffusion tensor and Ω given by (10), multiplication by $1, P_1, P_2, \ldots,$ and subsequent integration over d^2u yields the following set of "diffusion-relaxation" equations:

$$\frac{\partial n}{\partial t} - D \frac{\partial^2}{\partial x^2} n = 0 , \tag{14}$$

$$\frac{\partial n_j}{\partial t} - D \frac{\partial^2}{\partial x^2} n_j + j(j+1)\, w\, n_j = 0 , \qquad j = 1, 2, \ldots . \tag{15}$$

In a spatially homogeneous system, the quantities n_j relax with the orientational relaxation times

$$\tau_j = [j(j+1)\, w]^{-1} . \tag{16}$$

For a steady state situation to be considered here, the solution of Eqs. (14), (15) which obey the boundary condition at plane I are ($n_{\mathrm{I}} \equiv n(0)$)

$$n(x) = n(0) + [n(L) - n(0)]\, x/L \tag{17}$$

$$n_j(x) = n_j(L) [\sinh(L\, l_j^{-1})] \sinh(x\, l_j^{-1}) . \tag{18}$$

The "mean free path" l_j is defined by

$$l_j^2 = D\, \tau_j = \frac{2}{j(j+1)} l_1^2 , \tag{19}$$

for τ_j cf. (16). The hydrodynamical values for D and imply $l_1^2 = \frac{2}{3}(R_{\mathrm{r}}^3/R_{\mathrm{t}})$ i.e. l_1 is a length which is of the order of the linear dimension of a diffusing molecule. In Fig. 2, $n_1(x)/n_1(L)$ is displayed as function of x/L for the case where, the ratio L/l_1 assumes the values 1, 3, and 9.

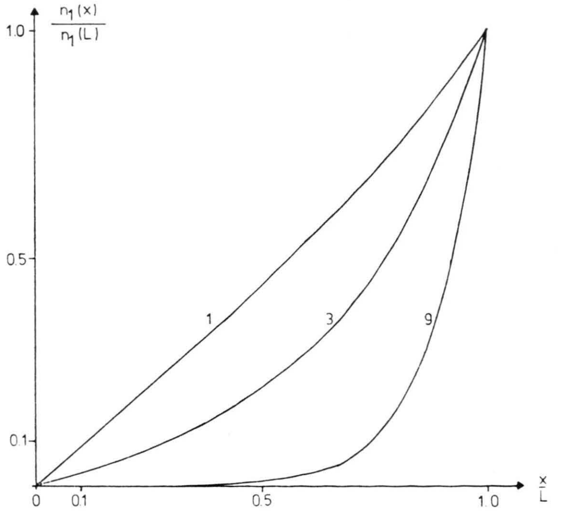

Fig. 2. The quantity $n_1(x)/n_1(L)$, cf. Eqs. (13), (18) as function of the dimensionless distance x/L. The curves are labelled with their pertaining value for L/l_1.

The value $n(L)$ of the number density and the values $n_j(L)$ of n_j at plane II have to be determined from the boundary condition (5). Before this is done, it is shown that the expression (8) for ν_{eff} can be cast into an alternative form which will be used in the following.

3. *Alternative Expression for the Effective Reaction Frequency*

Integration of Eq. (5) over the molecular orientation (i.e. over d^2u) and use of (17) leads to

$$- D L^{-1} [n(L) - n(0)] = l_0 \int \nu f \, d^2u .$$

Comparison with Eq. (8) (notice that $n_{\mathrm{I}} \equiv n(0)$) yields an alternative expression for the effective reaction frequency ν_{eff}, viz.

$$\nu_{\mathrm{eff}} = \nu_{\mathrm{D}} \left(1 - \frac{n(L)}{n(0)} \right) . \tag{20}$$

For $n(L) \to 0$, ν_{eff} approaches the value

$$\nu_{\mathrm{D}} = D (L\, l_0)^{-1} . \tag{21}$$

This corresponds to the completely diffusion dominated case which is realized when every molecule reacts practically instantly as soon as it enters the reaction volume of thickness l_0 at the reaction surface. The reaction rate coefficient pertaining to ν_{D} is (cf. Eq. (9))

$$k_{\mathrm{D}} = l_0\, F\, \nu_{\mathrm{D}} = D (F/L) , \tag{22}$$

where F is the area of the reaction surface. The expression (22) which is analogous to the v. Smoluchowsky rate coefficient [2] is independent of the reaction length l_0.

In general, $n(L)$ occurring in (20) is nonzero. It has to be determined from the boundary condition.

4. *Consequences of the Boundary Condition*

Before the boundary condition (5) at surface II can be applied, the dependence of the reaction frequency ν on the angle ϑ between $\boldsymbol{u}$ and $\boldsymbol{e}^x$ has to be specified. Here, the case

$$\nu = \nu_0 (1 + \beta \cos \vartheta) \tag{23}$$

is treated. The quantity β is a measure for the orientational selectivity of the reaction, ν_0 is the directional average of ν, see Figure 3. If no molecules re-enter the fluid at surface II, the quantity ν is positive. This implies $\nu_0 > 0$ and $-1 < \beta < 1$.

Insertion of the expansion (12) for the distribution function into the boundary condition (5) with

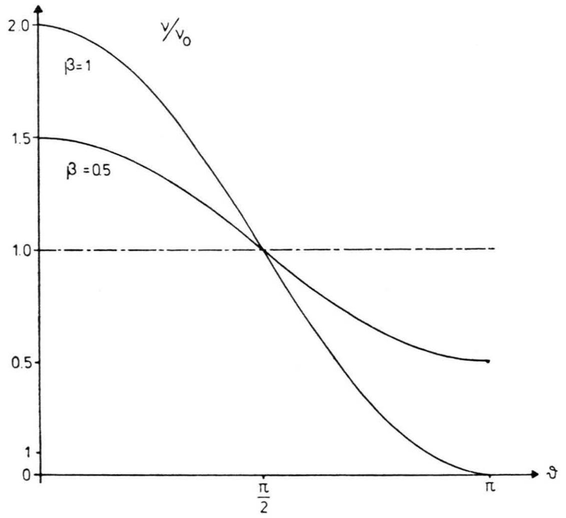

Fig. 3. The surface reaction frequency ν (divided by its orientational average ν_0) as given by Eq. (23) as function of the angle ϑ between the figure axis of a molecule and the surface normal. The parameter β is a measure for the orientational selectivity of the chemical reaction.

ν given by (23), multiplication of this relation by $1, P_1, P_2, \ldots$, subsequent integration over d^2u and use of (17), (18) leads to the boundary relations

$$-DL^{-1}[n(L)-n(0)] = \nu_0 l_0 [n(L) + \beta n_1(L)], \qquad (24)$$

$$-D l_j^{-1} n_j(L) \operatorname{ctgh}(L l_j^{-1}) = \nu_0 l_0 [n_j(L) + \beta j (2j+1)^{-1} n_{j-1}(L) + \beta (j+1)(2j+1)^{-1} n_{j+1}(L)], \qquad (25)$$
$$j = 1, 2, 3, \ldots .$$

Clearly, this is a set of coupled linear equations for $n(L)$, $n_j(L)$, the term containing $n(0)$ in (24) is considered as the inhomogeneity.

The set of Eqs. (24), (25) can be solved for $n(L)$ in terms of a continued fraction expansion. Incidentally, a similar mathematical problem is encountered in connection with the wave vector dependence of the diffusion coefficient in a gas [7]. With the abbreviations

$$K_0 = \nu_D/\nu_0 = D(L l_0 \nu_0)^{-1}, \qquad (26)$$

$$K_j = D(l_j l_0 \nu_0)^{-1} \operatorname{ctgh}(L l_j^{-1}), \quad j = 1, 2, \ldots, \qquad (27)$$

$$c_j = \frac{j^2}{(2j-1)(2j+1)} \cdot (1 + K_{j-1})^{-1} (1 + K_j)^{-1}, \qquad (28)$$

the relation

$$n(L)/n(0) = K_0 (1 + K_0)^{-1} H(\beta) \qquad (29)$$

is obtained where the function $H(\beta)$ is given by

$$H(\beta) = \frac{1|}{|1} + \frac{-c_1\beta^2|}{|1} + \frac{-c_2\beta^2|}{|1} + \cdots . \qquad (30)$$

In (30), the notation [8] $\frac{x_1|}{|y_1} + \frac{x_2|}{|y_2} \cdots$ is used for the continued fraction

$$\frac{x_1}{y_1 + \frac{x_2}{y_2 + \cdots}} .$$

Notice that H is an even function of β and that one has $H = 1$ for $\beta = 0$. The n-th approximant to H (corresponding to $c_j = 0$ for $j > n$) is denoted by $H^{(n)}$. In particular, one has

$$H^{(1)} = (1 - c_1 \beta^2)^{-1},$$
$$H^{(2)} = [1 - c_1 \beta^2 (1 - c_2 \beta^2)^{-1}]^{-1}. \qquad (31)$$

Insertion of (29) into (20) yields the desired expression for the effective reaction frequency ν_{eff}. The pertaining reaction rate then is given by $k_{\text{eff}} = l_0 F \nu_{\text{eff}}$, cf. Equation (9). These results can be expressed in the form

$$k^*(\beta) \equiv k_{\text{eff}}(\beta)\, k_D^{-1} = \nu_{\text{eff}}(\beta)\, \nu_D^{-1} = (1 + K_0)^{-1} [1 + K_0 (1 - H(\beta))], \qquad (32)$$

for ν_D and k_D see (21), (22). Clearly, the dimensionless quantity k^* is the ratio between the effective reaction rate k_{eff} and the completely diffusion dominated value k_D is given by (22).

III. Discussion

1. No Orientational Selectivity

For the case where the surface reaction frequency $\nu(\boldsymbol{u})$ is independent of the orientation of the molecules (i.e. $\nu = \nu_0$, $\beta = 0$, cf. Eq. (23)), Eq. (32) reduces to

$$k^*(0) = (1 + K_0)^{-1}. \qquad (33)$$

It is recalled that $K_0 = \nu_D \nu_0^{-1}$. With k_0 given by $k_0 = l_0 F \nu_0$ and the length L_0 defined by

$$L_0 = D(l_0 \nu_0)^{-1}, \qquad (34)$$

this quantity can also be expressed as

$$K_0 = k_D k_0^{-1} = L_0 L^{-1}. \qquad (35)$$

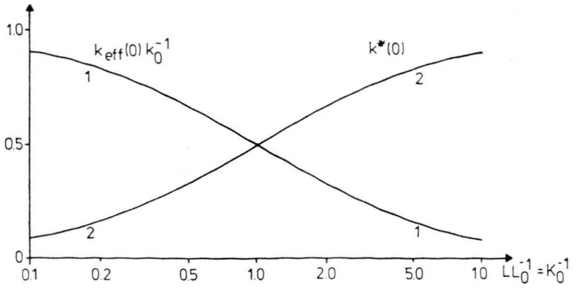

Fig. 4. The quantities $k_{\rm eff}\, k_0^{-1}$ (curve 1) and $k^* = k_{\rm eff}\, k_{\rm D}^{-1}$ (curve 2) for $\beta = 0$ as functions of the length L in units of L_0, cf. Equations (33), (34).

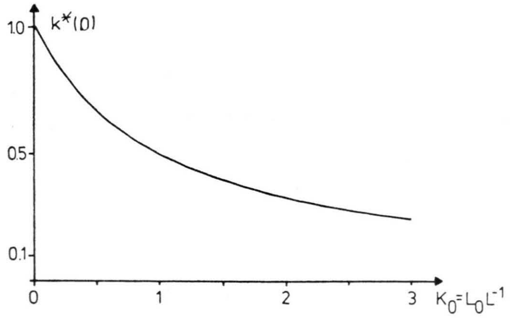

Fig. 5. The reduced reaction rate k^* for $\beta = 0$ as function of $K_0 = L_0\, L^{-1}$.

If the distance L between the plane where the diffusing molecules start and the reaction plane is very large compared with L_0 (this corresponds to $K_0 \ll 1$, $\nu_{\rm D} \ll \nu_0$) the reaction rate is practically determined by the diffusion process alone and $k_{\rm eff}$ approaches $k_{\rm D}$ (this corresponds to $k^* \to 1$). In the other limiting case, viz. $L \ll L_0$ ($K_0 \gg 1$, $\nu_{\rm D} \gg \nu_0$), the effective reaction rate approaches the value k_0.

In Fig. 4, $k_{\rm eff}(0)$ k_0^{-1} (curve 1) and $k^*(0)$ (curve 2) are plotted as function of $K_0^{-1} = LL_0^{-1}$. Since $k_{\rm eff}(0)$ decreases as L^{-1} for large values of L, k^* which is proportional to L $k_{\rm eff}$ becomes constant for $L \gg L_0$. In Fig. 5, $k^*(0)$ is displayed as function of $K_0 = L^{-1} L_0$. Notice that small values of K_0 correspond to the diffusion dominated regime.

Next, the more interesting case $\beta \neq 0$ is discussed in some detail.

2. *Influence of the Orientational Selectivity on the Effective Reaction Rate*

The influence of the orientational selectivity of the surface reaction associated with $\beta \neq 0$ on the effective reaction rate is best studied by considering the difference

$$\Delta k^* = k^*(\beta) - k^*(0)\,, \tag{36}$$

and the relative difference

$$\varepsilon = (k^*(0))^{-1} \Delta k^* = k_{\rm eff}(\beta)\, k_{\rm eff}^{-1}(0) - 1 \tag{37}$$

between the reaction rates for $\beta \neq 0$ and $\beta = 0$. From (32),

$$\begin{aligned} \varepsilon &= K_0 [1 - H(\beta)]\,, \\ \Delta k^* &= (1 + K_0)^{-1}\, \varepsilon \end{aligned} \tag{38}$$

is inferred. Due to $H(\beta) \geqq 1$, one has $k_{\rm eff}(\beta) < k_{\rm eff}(0)$ and $\Delta k^* < 0$, $\varepsilon < 0$, i.e. the orientational selectivity leads to a decrease of the effective reaction rate. The quantities Δk^* and ε depend on β, K_0, and on $L_0 l_j^{-1}$, cf. Equations (27)–(30). Since one has $l_j = \sqrt{2}\, [j(j+1)]^{-1/2} l_1$, the ratios $L_0 l_j^{-1}$ can be related to the quantity

$$q = L_0 l_1^{-1}\,. \tag{39}$$

Thus the relevant parameters are β, $K_0 = L_0 L^{-1}$, and q. In particular, the K_j, $j \geqq 1$, can be expressed in terms of q, viz.

$$K_j = \sqrt{\tfrac{1}{2} j(j+1)}\, q\, \mathrm{ctgh}\big(\sqrt{\tfrac{1}{2} j(j+1)}\, q\big)\,. \tag{40}$$

For given q, the physically meaningful range of K_0 is restricted to $K_0 \lesssim q$ corresponding to $L \gtrsim l_1$. It is recalled that l_1 is a length of the order of the linear dimension of a diffusing molecule (unless, at higher concentrations, collective phenomena lead to a kind of a pretransitional slowing down of the relaxation time τ_1 and consequently to a l_1 which is significantly larger than a molecular dimension [9]. The parameter L/l_1 occurring in connection with Fig. 2 is equal to $q K_0^{-1}$.

Next, it is noticed that the continued fraction for $H(\beta)$ which is needed in order to evaluate ε and Δk^* from (38) can be rewritten as

$$H(\beta) = [1 - \tfrac{1}{3}\beta^2 (1 + K_0)^{-1} (1 + K_1)^{-1} \alpha(\beta, q)]^{-1}, \tag{41}$$

with

$$\alpha(\beta, q) = \frac{1}{|1} - \frac{c_2 \beta^2|}{|1} - \frac{c_3 \beta^2|}{|1} - \cdots. \tag{42}$$

The quantities K_j with $j \geqq 2$ occurring in c_j (cf. Eq. (28)) are functions of q. The first approximant $H^{(1)}$ for H is obtained from (41) with $\alpha = 1$. Higher approximants $H^{(n)}$ are inferred from (41), (42) with $c_j = 0$ for $j > n$. The convergence of the continued fraction expansion for H is rather rapid. This is, e.g., reflected by the fact that the 2nd and 3rd approximations to α (cf. (42)) are 1.04225 and 1.04342 for $\beta = 1$ and $q = 1$. For $\beta = 1$ and $q = 3$, the 2nd approximation to α is 1.01083. For smaller values of β and larger values of q the convergence is even better. Thus in most cases it suffices to approximate α by the value $\alpha = 1$.

In Fig. 6, the quantities $-\varepsilon$ (dashed curves) and $-2\Delta k^*$ are plotted as functions of $K_0 = L_0 L^{-1}$ for $\beta = 1$. The upper curves pertain to $q = 1$; in particular, the curves labelled by (1) and (2) have been evaluated with the first and second approximations $H^{(1)}$ and $H^{(2)}$ for H. Higher approximations coincide with the curves (2) on the scale of the figure. For $q = 3$, these are the lower curves, the first approximation already yields the true value within the drawing accuracy. Notice that the relative deviation $-\varepsilon$ increases with increasing K_0 whereas the difference $-\Delta k^*$ between the values of k^* for $\beta \neq 0$ and $\beta = 0$ goes over a rather broad maximum at $K_0 = 1$.

Finally, in Fig. 7, $-\varepsilon$ is plotted as function of β for $K_0 = 1$. The curves pertaining to $q = 3$ and 9 are evaluated with the first approximation which practically coincides with the higher approximations. For $q = 1$, the two curves labelled by (1) and (2) are evaluated with the first and second approximants $H^{(1,2)}$ of $H(\beta)$. Clearly, even for $|\beta| = 1$ the difference between the two approximations is small and for $|\beta| \lesssim 0.7$ it can practically be disregarded.

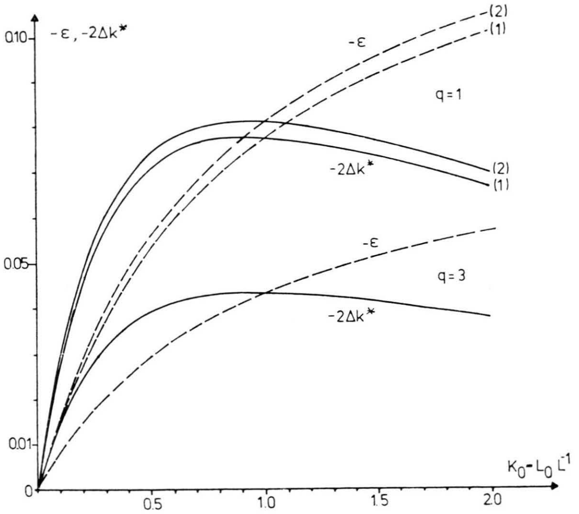

Fig. 6. The quantities $-\varepsilon$ (dashed curves) and $-2\Delta k^*$, cf. Eq. (38), as functions of $K_0 = L_0 L^{-1}$ for $\beta = 1$. The upper curves are for $q = L_0 l_1^{-1} = 1$ evaluated with the first (curves 1) and second (curves 2) approximants for H, cf. Equations (38), (41). The lower curves pertain to $q = 3$ evaluated in first approximation.

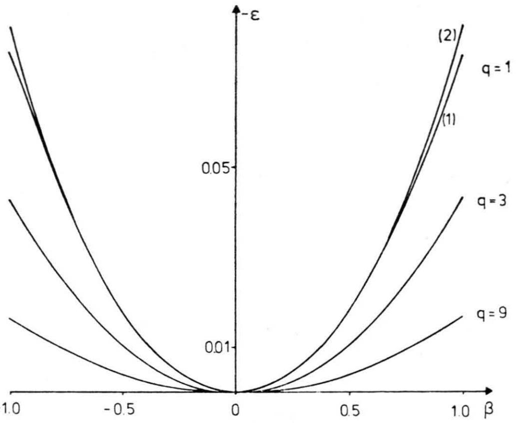

Fig. 7. The relative difference between the effective reaction rates for $\beta \neq 0$ and $\beta = 0$ as function of β for $K_0 = 1$. The curves for $q = 3$ and $q = 9$ are evaluated in first approximation, those for $q = 1$ are displayed in first (curve 1) and second approximation (curve 2).

Concluding Remarks

In this article, the influence of the orientational selectivity of a surface reaction on the diffusion controlled reaction rate has been studied with a special choice for the surface reaction frequency, cf. Equation (23). This has the advantage that the effective reaction frequency can be expressed in terms of a rather rapidly converging continued fraction. With a more general surface reaction frequency, recourse has to be made to a different solution method, e.g. a variational principle. From the present investigation, however, some conclusions can be drawn which should hold true in general. Close to the reaction surface, molecules with unfavorable orientation pile up in a layer which has a thickness of several "mean free path" l_1 as defined by Equation (19). The effect of this reaction induced alignment on the reaction rate can be disregarded if the distance L between the injection and reaction planes is very large compared with l_1. A second length scale, viz. L_0 as defined by Eq. (34), is of importance for the effective reaction rate. For $L \gg L_0$, the completely diffusion dominated situation, the effective reaction rate is given by a Smoluchowski type of expression with an orientation averaged reaction frequency. Effects associated with the reaction induced alignment become most pronounced for $L \approx L_0$. In the present case, the changes caused by the alignment are relatively small, cf. Figures 6, 7. This, however, might probably be different for a surface reaction where molecules in a narrower range of orientations are accepted.

Incidentally, it seems worthwile to consider reactive boundaries within the framework of the general theory of boundary conditions for transport-relaxation equations and for their underlying kinetic equation as developed by Waldmann [10].

Finally it deserves mentioning that the present investigations can be extended to study the influence of an orienting (electric or magnetic) field, as well as of the correlation between translational motion and orientation, on the diffusion controlled reaction rate.

[1] J. D. Watson, Molecular Biology of the Gene, Benjamin, New York 1970.

[2] R. M. Noyes, Progr. Reaction Kinet. **1**, 129 (1961); S. H. Lin, K. P. Li, and H. Eyring, Physical Chemistry, VII, 1, ed. H. Eyring, Academic Press, New York 1975.

[3] K. Solc and W. H. Stockmayer, J. Chem. Phys. **54**, 2981 (1971).

[4] R. Samson and J. M. Deutsch, J. Chem. Phys. **68**, 285 (1978).

[5] B. U. Felderhof and J. M. Deutsch, J. Chem. Phys. **64**, 4551 (1976); J. M. Deutsch, B. U. Felderhof, and M. J. Saxton, J. Chem. Phys. **64**, 4559 (1976).

[6] S. Hess, Physica **74**, 277 (1974).

[7] S. Hess, Z. Naturforsch. **32a**, 678 (1977).

[8] O. Perron, Die Lehre von den Kettenbrüchen, 3rd ed., vol. I and II, Teubner, Stuttgart 1954 und 1957.

[9] S. Hess, Z. Naturforsch. **31a**, 1034 (1976).

[10] L. Waldmann, Z. Naturforsch. **22a**, 1269 (1967); **32a**, 527 (1977); L. Waldmann and H. Vestner, Physica **80a**, 523 (1975).