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Intraparticle Diffusion Effects in Complex Systems of First Order Reactions

I. The Effects in Single Particles

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Any complex system of first order reactions connecting various chemical species may be uncoupled into an equivalent system of simple independent first order irreversible reactions of "characteristic" species. This mode of analysis provides a method for the determination of the effects of intraparticle diffusion on systems of first order reactions of arbitrary complexity. For isothermal systems obeying Fick's law of diffusion, the reaction rates in the presence of diffusion still remain linear functions of the concentrations ambient to the catalyst particles. Hence, in a kinetic experiment where the particle radii and the diffusivities remain constant, the experimental data will always appear to come from a consistent set of first order rate constants although they do not represent the *proper* rate constants for the *chemical* process. The method of analysis used also leads to good criteria for estimating whether diffusion effects can be neglected in a given system of reactions when either the rate constants or the rates of reaction are known. It also provides the transient solution when the diffusivities of the various species are equal so one may estimate the length of time required for a system to reach steady state. This is important for some systems, especially in the liquid phase, where hours may elapse before steady state is reached.

INTRODUCTION

Recent investigators, notably Thiele (*1*), Wheeler (*2*), Weisz and Prater (*3*), Weisz and Swegler (*4*), and Danckwerts (*5*) have shown how intraparticle diffusion of reactants and products within porous catalyst particles may modify greatly the behavior of such systems. These investigations have been restricted, however, to simple reactions consisting of, at most, two consecutive, irreversible steps; Thiele, Wheeler, and Weisz and Prater discuss such simple systems under steady state conditions, and Danckwerts discusses these systems with the steady state condition removed. It will be the purpose of this paper to discuss the behavior of systems of coupled first order reactions of arbitrary complexity, for both steady state and transient conditions, in the presence of intraparticle diffusion effects.

It has been shown recently by Wei and Prater (*6*) that, from both a mathematical and an experimental standpoint, any complex system of first order reactions may be uncoupled (except for certain trivial cases) into a set of independent first order irreversible reactions; hence one may consider such a complex system as a set of simple, independent systems. This may be illustrated by the three-component system of Fig. 1 where A_i is the ith molecular species, and B_i is the ith characteristic species in the equivalent set of uncoupled, independent reactions. The symbol k_{ij} designates the first order rate constant for the reaction from the species A_j to the species A_i, and λ_i is the rate constant for the irreversible decay of the characteristic species B_i. The species B_1 is the equilibrium species and does not change with time. The remainder of the

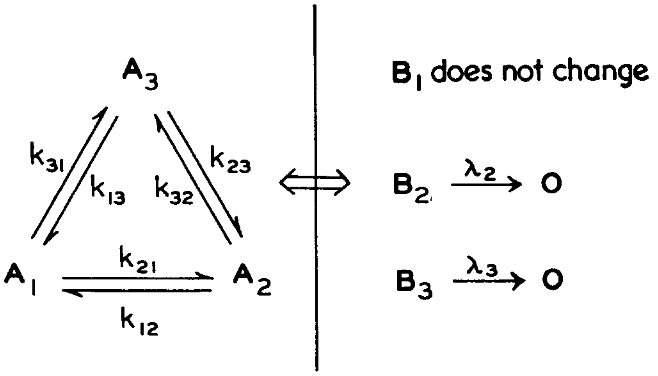


Fig. 1. The equivalence of coupled and uncoupled reaction systems.

characteristic species, B_2 and B_3, may be interpreted, physically, as "transference units," i.e., as special linear, fixed combinations of molecular species that react as packaged units. They are conceptually similar to the normal modes in vibration analysis and to wave functions in quantum mechanical systems.

Each of the species, B_2 and B_3, is related to a straight line reaction path as illustrated in Fig. 2. These straight line reactions paths, B'_2, B'_3, are used as a set of oblique coordinate axes to represent any composition as shown in Fig. 3. The point P is a mixture of a_1 parts of the molecular species A_1, a_2 parts of A_2, and a_3 parts of A_3; it may also be considered to be a mixture of b_1 parts of the equilibrium species B_1, b_2 parts of the characteristic species B_2, and b_3 parts of the characteristic species B_3. The full justification for, and treatment of, this method has been given by Wei and Prater (*6*).

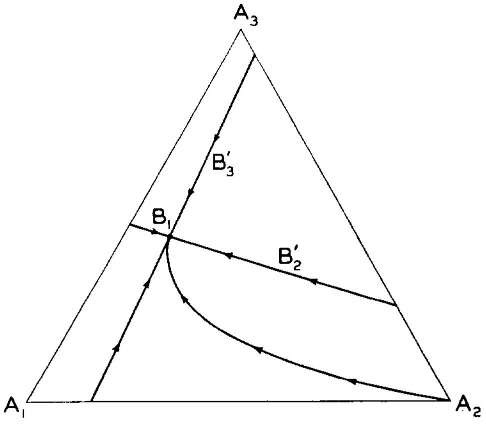


Fig. 2. The straight line reaction paths.

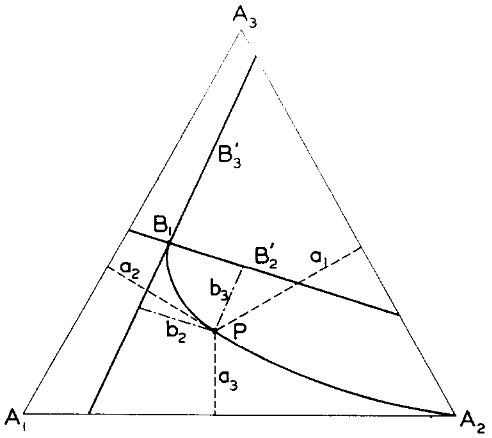


Fig. 3. The straight line reaction paths as oblique coordinate axes.

A similar transformation may also be used to obtain the solution for systems of first order reactions in the presence of intraparticle diffusion effects that obey Fick's law of diffusion. In the characteristic or B system of species, each species satisfies a simple and independent differential equation for diffusion with an irreversible sink. Thus, the problem may be solved by transforming to the B system of species, solving the set of independent differential equations obtained, and then transforming the results back to the molecular or A system of species.

II. The Over-all Steady State Reaction Rate of a Single Particle

A. General Discussion

1. *The Equation for the System and the Concept of Uncoupling*

Let us consider a complex system of first order reactions involving n molecular species A_i and occurring within a porous catalyst particle. At a point represented by the vector $\mathbf{r}$ within the catalyst particle, the local reaction rate for the species A_i is determined, in terms of the local concentrations $a_j(\mathbf{r})$ of the various species A_j, by

$$\sum_{j=1}^{n}{}' \left[k_{ij}a_j(\mathbf{r}) - k_{ji}a_i(\mathbf{r})\right]$$

Again the symbol k_{ij} designates the first order rate constant (many of which may be zero) for the reaction from species A_j to the species A_i. Since there are no rate constants of the form k_{ii}, the prime on the summation sign is used to signify that the index j goes from 1 to n skipping i. On the other hand, the rate of supply of the species A_i to the point $\mathbf{r}$ is given by $D_i\nabla^2 a_i(\mathbf{r})$ if the diffusivity D_i is independent of the concentration; this is true in the Knudsen range and is often a sufficiently good approximation for the gaseous diffusion range. When steady state conditions exist at the point $\mathbf{r}$, the reaction rate for the species A_i must equal its rate of supply by diffusion. Hence, for each species A_i, one has

$$-D_i\nabla^2 a_i(\mathbf{r}) = \sum_{j=1}^{n}{}' \left[k_{ij}a_j(\mathbf{r}) - k_{ji}a_i(\mathbf{r})\right] \qquad (1)$$

There are n of these equations and all of them may be written simultaneously as a single equation by using matrix notation;

$$\mathbf{D}\nabla^2\mathbf{a}(\mathbf{r}) = \mathbf{K}\mathbf{a}(\mathbf{r}) \qquad (2)$$

In Eq. (2), $\mathbf{a}$ is the composition vector with elements given by $a_1, a_2, \ldots, a_n$ and written as a column matrix. In general, each of the elements may freely assume a value of zero or a positive number. The domain of values that the vector $\mathbf{a}$ may assume constitutes the composition space, and it has n dimensions—one for each species A_i. In Eq. (2), $\mathbf{D}$ is the diagonal matrix

$$\begin{pmatrix} D_1 & 0 & \cdot & \cdot & \cdot & 0 \\ 0 & D_2 & \cdot & \cdot & \cdot & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & \cdot & \cdot & \cdot & D_n \end{pmatrix}$$

and $\mathbf{K}$ is the matrix

$$\begin{pmatrix} \sum_j' k_{j1} & -k_{12} & -k_{13} & \cdot & \cdot & -k_{1n} \\ -k_{21} & \sum_j' k_{j2} & -k_{23} & \cdot & \cdot & -k_{2n} \\ -k_{31} & -k_{32} & \sum_j' k_{j3} & \cdot & \cdot & -k_{3n} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ -k_{n1} & -k_{n2} & -k_{n3} & \cdot & \cdot & \sum_j' k_{jn} \end{pmatrix}$$

Multiplying Eq. (2) by the inverse matrix $\mathbf{D}^{-1}$, one obtains

$$\nabla^2\mathbf{a}(\mathbf{r}) = \mathbf{D}^{-1}\mathbf{K}\mathbf{a}(\mathbf{r}) \qquad (3)$$

Let the ambient concentrations, $\mathbf{a}(\mathbf{R})$, be uniform over the boundary of the particle. Using Eq. (3), one wishes to determine the over-all reaction rate for the whole particle expressed in terms of these ambient concentrations. It will be shown that even in a diffusion-controlled process, one can formally express the over-all rate of the reaction as $\dot{\mathbf{a}}_D = -\mathbf{K}^{\dagger}\mathbf{a}(\mathbf{R})$ where $\mathbf{K}^{\dagger}$ is a diffusion-disguised over-all rate matrix. We shall show now how $\mathbf{K}^{\dagger}$ is related to $\mathbf{D}$ and $\mathbf{K}$.

Let us compare Eq. (3) with the equation studied by Wei and Prater (*6*) for the reaction rates of systems in which the diffusion transport of reactants is unimportant. In the latter formulation, solutions are sought for the matrix equation

$$d[\mathbf{a}(t)]/dt = -\mathbf{K}\mathbf{a}(t) \qquad (4)$$

This equation gives the movement of the composition vector $\mathbf{a}(t)$ in the composition space. Wei and Prater (*6*) show that a transformation, which changes Eq. (4) into the equation

$$d[\mathbf{b}(t)]/dt = -\mathbf{\Lambda}\mathbf{b}(t) \qquad (5)$$

can be determined from the measured equilibrium composition and the location of the straight line reaction paths. In Eq. (5), the vector $\mathbf{b}(t)$ is the composition vector expressed in terms of the characteristic species and $\mathbf{\Lambda}$ is a diagonal matrix with elements that are nonnegative (zero or positive) real numbers; these elements are the rate constants for the B system of species. The transformation changes the highly coupled system of molecular species into the equivalent uncoupled system of characteristic species B_i as given above and represents an extensive simplification of the problem. The transformation gives the relations

$$\mathbf{\Lambda} = \mathbf{X}^{-1}\mathbf{K}\mathbf{X} \tag{6}$$

and

$$\mathbf{b}(t) = \mathbf{X}^{-1}\mathbf{a}(t) \tag{7}$$

where $\mathbf{X}$ is the matrix formed by the characteristic vectors of the matrix $\mathbf{K}$, and $\mathbf{X}^{-1}$ is the inverse of the matrix $\mathbf{X}$. The transformation matrix $\mathbf{X}$ may be determined experimentally from the equilibrium composition and the location of straight line reaction paths in composition space. Equation (6) shows that the rate constants, λ_i, for the B system of species, which form the diagonal elements of the matrix $\mathbf{\Lambda}$, are the characteristic values of the matrix $\mathbf{K}$.

It will be shown that Eq. (3) can be transformed in an analogous manner into the equation

$$\nabla^2\mathbf{b}(\mathbf{r}) = \mathbf{\Phi}\mathbf{b}(\mathbf{r}) \tag{8}$$

where the matrix $\mathbf{\Phi}$ is again a diagonal matrix with elements that are nonnegative real numbers; this also transforms the coupled system into an uncoupled system of characteristic species and again the problem is greatly simplified. Using the solutions obtained by means of the transformation, the over-all reaction rates are obtained from the fluxes of the reactants across the boundary of the particle. These fluxes will be shown to be linear functions of the ambient concentrations such that the over-all rate of reaction of the species A_i per unit volume of catalyst is $\Sigma'_{j=1}[k_{ij}{}^{\dagger}a_j(\mathbf{R}) - k_{ji}{}^{\dagger}a_i(\mathbf{R})]$. The constants, $k_{ij}{}^{\dagger}$, are the diffusion-disguised rate constants and are functions only of the intrinsic rate constants k_{ij}, the diffusivities D_i, and the particle geometry; they are independent of the ambient concentrations.

2. A Constraint on the System

Before presenting the details of the transformation of Eq. (3) into Eq. (8), let us examine an important constraint that arises in these systems. For systems of first order reactions in the absence of diffusion effects, the quantity $\Sigma_i a_i(t)$ is invariant with time. This quantity, which derives from the law of conservation of mass, is an important constraint for these systems (*6*). For an n-component system, it restricts the movement of the end of the composition vector $\mathbf{a}(t)$ to an $(n - 1)$-dimensional "plane" in the n-dimensional composition space. An example of such a "plane" is shown in Fig. 2 for a three component system; the reaction paths show the movements of the ends of the composition vectors in this plane. Let us examine the nature of the corresponding invariant with respect to the space variable $\mathbf{r}$ for systems in which diffusion transport is important. The law of conservation of mass requires that the total rate of reaction be zero at any point $\mathbf{r}$. On the other hand, the steady state condition requires that the diffusion transport of each species A_i exactly balances the rate of reaction of this species. Hence, summing Eq. (1) over all species A_i and applying the condition that the sum of all rates is equal to zero at any point, one obtains

$$\nabla^2 \Sigma_i D_i a_i(\mathbf{r}) = 0 \tag{9}$$

for all values of $\mathbf{r}$. Let the concentrations $a_j(\mathbf{R})$, which corresponds to the ambient concentrations, be constant over the boundary of the particle. Then one obtains the result that

$$\Sigma_i D_i a_i(\mathbf{r}) = \Sigma_i D_i a_i(\mathbf{R}) \tag{10}$$

since any quantity that obeys Laplace's equation and has a constant value over the boundary has this same constant value throughout the region of space enclosed by the boundary (*7*).

If the diffusivities, D_i, are *not* functions of the concentrations, and therefore also *not* of position, the quantity $\Sigma_i a_i(\mathbf{r})$ cannot be invariant with respect to the space variable unless the diffusivities of all species are equal. This means that, for reactions in the gaseous phase, the total pressure cannot be constant throughout the particle and must be a function of **r**. In the Knudsen range of diffusivities, one gaseous molecule seldom collides with another gaseous molecule, and the pressure at any point need not equal the ambient pressure.

The constraint, $\Sigma_i D_i a_i$ = constant, confines the composition vector **a** to an $(n - 1)$-dimensional subspace of the n-dimensional composition space and therefore reduces the dimensions of the problem. In some cases, for example for the system $A_1 \rightleftarrows A_2 \rightarrow A_3$, the constraint reduces the dimension of the problem sufficiently so that explicit solutions can be obtained by ordinary methods.

3. The Properties of the Characteristic Values

Let us begin the detailed discussion of Eq. (3) by showing that the matrix $\mathbf{D}^{-1}\mathbf{K}$ has only real nonnegative characteristic values. Let $\mathbf{A}^*$ be the diagonal matrix whose diagonal elements are the equilibrium values a_1^*, a_2^*, . . . , and a_n^* of the components A_1, A_2, . . . , and A_n. The principle of microscopic reversibility requires the matrix $\mathbf{KA}^*$ to be symmetric (*6*). Using the matrices $[(\mathbf{A}^*)^{-1}\mathbf{D}]^{1/2}$ and $[(\mathbf{A}^*)^{-1}\mathbf{D}]^{-1/2}$ to make a similarity transformation on the matrix $\mathbf{D}^{-1}\mathbf{K}$, one obtains

$$[(\mathbf{A}^*)^{-1}\mathbf{D}]^{1/2}[\mathbf{D}^{-1}\mathbf{K}][(\mathbf{A}^*)^{-1}\mathbf{D}]^{-1/2} = [\mathbf{A}^*\mathbf{D}]^{-1/2}[\mathbf{KA}^*][\mathbf{A}^*\mathbf{D}]^{-1/2} \quad (11)$$

since the diagonal matrices $\mathbf{A}^*$ and $\mathbf{D}$ commute so that $(\mathbf{A}^*\mathbf{D})^{1/2} = (\mathbf{A}^*)^{1/2}\mathbf{D}^{1/2}$. Since $\mathbf{KA}^*$ is a symmetric matrix, one has

$$[(\mathbf{A}^*\mathbf{D})^{-1/2}(\mathbf{KA}^*)(\mathbf{A}^*\mathbf{D})^{-1/2}]^T = (\mathbf{A}^*\mathbf{D})^{-1/2}(\mathbf{KA}^*)(\mathbf{A}^*\mathbf{D})^{-1/2} \quad (12)$$

where T signifies the transpose. The matrix given by the right side of Eq. (11) is equal to its transpose and is therefore symmetric; hence the matrix given by the left side of Eq. (11) is also symmetric. Since the matrix $\mathbf{D}^{-1}\mathbf{K}$ is similar to a symmetric matrix, it can have only real characteristic values (*8*). The similarity relation

$$\mathbf{D}^{-1}\mathbf{K} \sim (\mathbf{A}^*\mathbf{D})^{-1/2}(\mathbf{KA}^*)(\mathbf{A}^*\mathbf{D})^{-1/2}$$

may also be used to show that the characteristic values of the matrix $\mathbf{D}^{-1}\mathbf{K}$ are nonnegative numbers. Wei and Prater (*6*) give proof that the matrix $\mathbf{KA}^*$ has nonnegative characteristic values. Then the matrix $\mathbf{Q}^T(\mathbf{KA}^*)\mathbf{Q}$ must also have only nonnegative characteristic values since it is a positive quadratic form for any matrix $\mathbf{Q}$. Hence, the matrix $(\mathbf{A}^*\mathbf{D})^{-1/2}(\mathbf{KA}^*)(\mathbf{A}^*\mathbf{D})^{-1/2}$, and consequently, the matrix $\mathbf{D}^{-1}\mathbf{K}$ can have only real nonnegative characteristic values.

4. The Transformation

Let us now examine the details of the transformation of Eq. (3) into Eq. (8). Let $\mathbf{Y}$ be the matrix formed from the characteristic vectors of the matrix $\mathbf{D}^{-1}\mathbf{K}$. Then,

$$\mathbf{\Phi} = \mathbf{Y}^{-1}\mathbf{D}^{-1}\mathbf{KY} \quad (13)$$

where $\mathbf{\Phi}$ is a diagonal matrix whose elements are the real characteristic values of the matrix $\mathbf{D}^{-1}\mathbf{K}$. Thus,

$$\mathbf{D}^{-1}\mathbf{K} = \mathbf{Y\Phi Y}^{-1} \quad (14)$$

The substitution of Eq. (14) into Eq. (3) gives

$$\nabla^2\mathbf{a}(\mathbf{r}) = \mathbf{Y\Phi Y}^{-1}\mathbf{a}(\mathbf{r}) \quad (15)$$

The multiplication of Eq. (15) from the left by $\mathbf{Y}^{-1}$ gives

$$\nabla^2\mathbf{Y}^{-1}\mathbf{a}(\mathbf{r}) = \mathbf{\Phi Y}^{-1}\mathbf{a}(\mathbf{r}) \quad (16)$$

since the matrix $\mathbf{Y}^{-1}$ is constant and may be moved to the right of the operator ∇^2. Let

$$\mathbf{b}(\mathbf{r}) = \mathbf{Y}^{-1}\mathbf{a}(\mathbf{r}) \quad (17)$$

then Eq. (16) becomes

$$\nabla^2\mathbf{b}(\mathbf{r}) = \mathbf{\Phi b}(\mathbf{r}) \quad (18)$$

which is identical with Eq. (8). Since the matrix $\mathbf{\Phi}$ is diagonal, Eq. (18) is equivalent to the set of n independent scalar equations of the form

$$\nabla^2 b_j(\mathbf{r}) = \Phi_j b_j(\mathbf{r}) \quad (19)$$

Equation (19) is the differential equation for diffusion in the presence of a sink that is a single first order irreversible reaction. Hence, the steady state solution for the problem of complex systems of first order reactions with diffusion transport can be obtained for any geometry for which the solution of Eq. (19) is known. The remainder of this discussion will be confined to diffusion in a spherical particle since other geometries for which the solution of Eq. (19) is known may be obtained in an analogous manner.

B. The Solution for a Spherical Particle

For a spherical particle, it will be convenient to define a new diagonal matrix with nonnegative elements such that

$$\mathbf{\Phi} = (1/R)^2 \boldsymbol{\varphi}^2 \tag{20}$$

i.e., such that the elements φ_j of the matrix $\boldsymbol{\varphi}$ are given by

$$\varphi_j = (+\sqrt{\Phi_j})R \tag{21}$$

As for the matrix $\mathbf{K}$ in systems of first order reactions in which diffusion effects are negligible, the matrix $\mathbf{D}^{-1}\mathbf{K}$ has one characteristic value equal to zero; this corresponds to the equilibrium species which does not react and therefore has no diffusion effect associated with it. Each of the other characteristic species has its own parameter φ_j analogous to $R(+\sqrt{k/D})$ for the simple irreversible reactions studied by other investigators (*1–5*). Furthermore, each characteristic species will have its own effectiveness factor η_j analogous to the corresponding quantity as defined for the simple systems.

The solution for the scalar Eq. (19) for a spherical geometry is

$$b_j(r) = (R/r)\frac{\sinh \varphi_j(r/R)}{\sinh \varphi_j} b_j(R) \tag{22}$$

Thus we see from Eq. (17) that the concentration profile of any species, $a_i(r)$, is a sum of terms of the form of Eq. (22). The total reaction rate for a single particle can now be evaluated by computing the total flux across the boundary of the particle from the gradient of $b_j(r)$ evaluated at the boundary R. The gradient at R is given by

$$\frac{d}{dr} b_j(r)|_R = (1/R)(\varphi_j \coth \varphi_j - 1)b_j(R), \qquad j = 1 \text{ to } n \tag{23}$$

The set of n equations given by (23) may be written as a single matrix equation;

$$\frac{d}{dr}\mathbf{b}(r)|_R = (1/R)(\boldsymbol{\varphi} \coth \boldsymbol{\varphi} - \mathbf{I})\mathbf{b}(R) \tag{24}$$

where $\mathbf{I}$ is the identity matrix, and $\coth \boldsymbol{\varphi}$ is a diagonal matrix with diagonal elements $\{\coth \varphi_1, \coth \varphi_2, \ldots, \coth \varphi_n\}$. Transforming the characteristic system of species into the molecular system of species by the use of the transformation given by Eq. (17) and multiplying from the left by the matrix $\mathbf{Y}$, one obtains

$$\frac{d}{dr}\mathbf{a}(r)|_R = (1/R)\mathbf{Y}(\boldsymbol{\varphi} \coth \boldsymbol{\varphi} - \mathbf{I})\mathbf{Y}^{-1}\mathbf{a}(R) \tag{25}$$

Hence, the rate of reaction per unit volume of catalyst is given by

$$\frac{-4\pi R^2 \mathbf{D}\left[\frac{d}{dr}\mathbf{a}(r)|_R\right]}{4/3\pi R^3} = -(3/R^2)\mathbf{D}\mathbf{Y}(\boldsymbol{\varphi} \coth \boldsymbol{\varphi} - \mathbf{I})\mathbf{Y}^{-1}\mathbf{a}(R) \tag{26}$$

Following the notation of Weisz and Prater (*3*), one defines the diagonal matrices $\boldsymbol{\eta}$ and $\boldsymbol{\theta}$ so that

$$\boldsymbol{\eta} = 3\boldsymbol{\varphi}^{-2}(\boldsymbol{\varphi} \coth \boldsymbol{\varphi} - \mathbf{I}) \tag{27}$$

and

$$\boldsymbol{\theta} = \boldsymbol{\varphi}^2\boldsymbol{\eta} = 3(\boldsymbol{\varphi} \coth \boldsymbol{\varphi} - \mathbf{I}) \tag{28}$$

The elements η_i of the matrix $\boldsymbol{\eta}$ are dimensionless quantities that give the fractional reduction, caused by diffusion transport, of the rate of reaction of the *i*th characteristic species B_i. In Eq. (27), the matrix $\boldsymbol{\varphi}^{-2}$ is a diagonal matrix with diagonal elements given by $\{0, 1/\varphi_2^2, \ldots, 1/\varphi_n^2\}$. Although the matrix $\boldsymbol{\varphi}^2$ is singular and has no proper inverse, it is often convenient to define a generalized inverse as given by $\boldsymbol{\varphi}^{-2}$ [see for example ref. (*8*)]. The rate of reaction per unit volume of catalyst in the presence of diffusion effects is then given by

$$\dot{\mathbf{a}}_D = -(1/R^2)\mathbf{D}\mathbf{Y}\boldsymbol{\varphi}^2\boldsymbol{\eta}\mathbf{Y}^{-1}\mathbf{a}(R) \tag{29}$$

$$= -(1/R^2)\mathbf{D}\mathbf{Y}\boldsymbol{\theta}\mathbf{Y}^{-1}\mathbf{a}(R) \tag{30}$$

$$= -\mathbf{K}^\dagger\mathbf{a}(R) \tag{31}$$

where

$$\mathbf{K}^\dagger = (1/R^2)\mathbf{D}\mathbf{Y}\boldsymbol{\theta}\mathbf{Y}^{-1} = \mathbf{X}^\dagger\mathbf{\Lambda}^\dagger(\mathbf{X}^\dagger)^{-1} \tag{32}$$

The matrix $\mathbf{K}^\dagger$ is the diffusion-disguised, over-all rate constant matrix based on the ambient concentrations $\mathbf{a}(R)$; the matrices $\mathbf{X}^\dagger$ and $\mathbf{\Lambda}^\dagger$ are the diffusion-disguised matrices of characteristic vectors and rate constants, respectively. The matrix $\mathbf{X}^\dagger$ is determined experimentally from the equilibrium composition and the location of the straight line reaction paths, and the matrix $\mathbf{\Lambda}^\dagger$ is determined by the rate of reaction of each characteristic species. Equation (32) shows that the matrix $\mathbf{K}^\dagger$ depends only on the intrinsic rate constants k_{ij} and the diffusivities D_i and not on the ambient concentrations.

If Eq. (32) is multiplied from the left by the matrix $\mathbf{D}^{-1}$, one obtains

$$\mathbf{D}^{-1}\mathbf{K}^\dagger = (1/R^2)\mathbf{Y}\boldsymbol{\theta}\mathbf{Y}^{-1} \qquad (33)$$

Hence, the matrices $\mathbf{D}^{-1}\mathbf{K}$ and $\mathbf{D}^{-1}\mathbf{K}^\dagger$ have the same characteristic vectors but different characteristic values—namely, $\boldsymbol{\varphi}^2/R^2$ and $\boldsymbol{\theta}/R^2$, respectively.

Three sets of characteristic vectors have been introduced:

(1) The set $\mathbf{X}$ is associated with the intrinsic rate matrix $\mathbf{K}$, and is related to the straight line reaction paths when diffusion effects are negligible.
(2) The set $\mathbf{Y}$ is associated with the matrices $\mathbf{D}^{-1}\mathbf{K}$ and $\mathbf{D}^{-1}\mathbf{K}^\dagger$, and is related to the concentration profile inside the particle.
(3) The set $\mathbf{X}^\dagger$ is associated with the diffusion-disguised rate matrix $\mathbf{K}^\dagger$, and is related to the straight line reaction paths for the entire particle when diffusion effects are appreciable. The diffusion-disguised rate matrix $\mathbf{K}^\dagger$ is reduced to the true rate matrix $\mathbf{K}$ when D_i/R^2 approaches infinity for all i.

The set of characteristic vectors given by the matrix $\mathbf{X}^\dagger$ are the ones directly measured in the laboratory and the sets given by $\mathbf{Y}$ and $\mathbf{X}$ are calculated using $\mathbf{X}^\dagger$. But, if the diffusivities, D_i, for all the molecular species are equal, the matrix $\mathbf{D}^{-1}$ reduces to a scalar quantity, $1/D$, and a great simplification takes place since $\mathbf{X}^\dagger = \mathbf{Y} = \mathbf{X}$. In this case, the following equations replace the more complicated Eqs. (20) and (32):

$$\boldsymbol{\varphi}^2 = (R^2/D)\mathbf{\Lambda} \qquad (20a)$$

and

$$\mathbf{K}^\dagger = \mathbf{X}\mathbf{\Lambda}\boldsymbol{\eta}\mathbf{X}^{-1} \qquad (32a)$$

When the matrices $\mathbf{K}^\dagger$ and $\mathbf{D}$ have been measured, the matrix $\mathbf{K}$ can be computed. By combining Eqs. (28), (20a), and (32a), one obtains the diagonal matrix

$$\boldsymbol{\theta} = (D/R^2)\mathbf{X}^{-1}\mathbf{K}^\dagger\mathbf{X} = 3(\boldsymbol{\varphi}\coth\boldsymbol{\varphi} - \mathbf{I})$$

The value of each θ_i can be calculated from a knowledge of $\mathbf{K}^\dagger$ and $\mathbf{D}$. The value of each φ_i is then calculated by the equation

$$\theta_i = 3(\varphi_i \coth \varphi_i - 1)$$

Then one solves for each λ_i by the equation

$$\lambda_i = D\varphi_i^2/R^2$$

Then one obtains $\mathbf{K} = \mathbf{X}\mathbf{\Lambda}\mathbf{X}^{-1}$.

Let us compare the matrix Eq. (32) with with the corresponding expression for a single irreversible reaction. which is given by

$$k^\dagger = k\eta = (3k/\varphi^2)(\varphi \coth \varphi - 1) = (D/R^2)\varphi^2\eta = (D/R^2)\theta \qquad (34)$$

This suggests a general alternate formulation that more closely resembles the formulation for the simple irreversible system. Instead of defining the matrix $\boldsymbol{\varphi}^2$ to be a diagonal matrix, one may define the nondiagonal matrix

$$\bar{\boldsymbol{\varphi}}^2 \equiv \mathrm{R}^2\mathbf{D}^{-1}\mathbf{K} \qquad (35)$$

The matrix $\mathbf{K}$ is singular and does not possess a proper inverse. Nevertheless, one may define, as before, a generalized inverse given by

$$\mathbf{K}^{-1} = \mathbf{X}\mathbf{\Lambda}^{-1}\mathbf{X}^{-1} \qquad (36)$$

where $\mathbf{\Lambda}^{-1}$ is the diagonal matrix with diagonal elements $[0, 1/\lambda_2, \ldots, 1/\lambda_n]$. In this case, one may define the nondiagonal matrix $\bar{\boldsymbol{\eta}}$

$$\bar{\boldsymbol{\eta}} \equiv 3\bar{\boldsymbol{\varphi}}^{-2}(\bar{\boldsymbol{\varphi}} \coth \bar{\boldsymbol{\varphi}} - \mathbf{I}) \qquad (37)$$

where $\coth \bar{\boldsymbol{\varphi}}$ is a matrix function of the matrix $\bar{\boldsymbol{\varphi}}$ (7). Then, the diffusion-disguised rate constant matrix is

$$\mathbf{K}^\dagger = \mathbf{K}\bar{\boldsymbol{\eta}}$$

This formulation is more compact, and the matrices $\mathbf{K}$, $\bar{\boldsymbol{\varphi}}$, and $\bar{\boldsymbol{\eta}}$ are handled in a manner that is almost identical to that of their scalar counterparts k, φ, and η.

C. Criteria for the Presence of Appreciable Diffusion Effects in Complex Systems of First Order Reactions In Spherical Particles

1. A Criterion Based on Rate Constants

Let the elements of the matrix $\boldsymbol{\varphi}$ be arranged in order so that $\varphi_1 = 0 \leqslant \varphi_2 \leqslant \varphi_3 \leqslant$

... $\leqslant \varphi_n$. The extent of the diffusion effect η_j, for each characteristic species B_j is given by the elements of the matrix Eq. (27), which are functions of φ_j; the smallest value of η is obtained when φ_j is φ_n. Thus any criterion that gives an upper limit for the characteristic values of the matrix $\mathbf{D}^{-1}\mathbf{K}$ will give an estimate of the lower limit for η_n and hence an estimate for the extent of the diffusion effect on the most sensitive characteristic species of the matrix $\mathbf{D}^{-1}\mathbf{K}$. An upper limit for the characteristic values may be obtained from the criterion

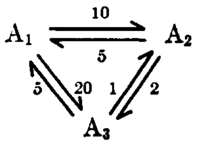
$$(\varphi_n/R)^2 \leqslant \text{maximum over } i \text{ of } \Sigma_j{}' \, (k_{ij} + k_{ji})/D_i \qquad (38)$$

This says, that for each species A_i, the values of all the rate constants leading towards and away from the species A_i are summed and then divided by the diffusivity of A_i. There are n such numbers, one for each molecular species; the value of $(\varphi_n/R)^2$ is less than or equal to the largest of these n numbers. In most cases, this estimate will be a pessimistic over-estimate of the upper limit. Where the diffusivities of the species are widely different, the following criterion may yield a smaller value:

$$(\varphi_n/R)^2 \leqslant \sum_{ij}\sum{}' \, k_{ji}/D_i \qquad (39)$$

In any case the value of $(\varphi_n/R)^2$ must be less than or equal to the smaller of the two estimates. Since the characteristic species behave as completely uncoupled reactants, the value of φ_n for which diffusion effects become negligible is identical with the results obtained with a simple irreversible system involving a single molecular species. Thus, if $\varphi_n \leqslant 1$, diffusion effects may be neglected [see for example Weisz and Prater, ref. (*3*)].

As an example let us examine the reaction system



with diffusivities $D_1 = 5$, $D_2 = 2$, and $D_3 = 4$. Equation (38) gives for each of the three species A_i

A₁: $(10 + 5 + 20 + 5)/5 = 8$
A₂: $(10 + 5 + 1 + 2)/2 = 9$
A₃: $(20 + 5 + 1 + 2)/4 = 7$

On the other hand, Eq. (39) gives

$$(10 + 20)/5 + (5 + 2)/2 + (1 + 5)/4 = 11$$

Thus the value of $(\varphi_n/R)^2$ is less than or equal to 9; the correct value is actually 7.8.

The rate constant matrix determined in the laboratory is the matrix $\mathbf{K}^\dagger$ and it is this matrix that must, in most cases, be used to test for the presence of significant diffusion effects. The characteristic values of the matrix $\mathbf{D}^{-1}\mathbf{K}^\dagger$ are θ_j/R^2 and correspond to the same system of characteristic species as obtained with the matrix $\mathbf{D}^{-1}\mathbf{K}$. Furthermore they are ordered in exactly the same way as the elements of the matrix $\boldsymbol{\varphi}$, that is, the characteristic value corresponding to the characteristic species B_n is the largest and will give a criterion for estimating the extent of diffusion effect for the most sensitive species. A modification of Eqs. (38) and (39) may be used in which $\varphi_n{}^2/R^2$ is replaced by θ_n/R^2 and the rate constants k_{ij} are replaced by the rate constants $k_{ij}{}^\dagger$. A criterion for negligible diffusion effects in a simple irreversible reaction system with a single species is given by Weisz and Prater (*3*) to be that $\theta \leqslant 1$. This same criterion can be used to test whether the matrix $\mathbf{K}^\dagger$ is a good approximation of the matrix $\mathbf{K}$.

2. A Criterion Based on Measured Reaction Rates

The quantity θ was defined by Weisz and Prater (*3*) for a single step in order to formulate a diffusion criterion in terms of observed *rates* of reaction instead of in terms of observed rate constants. Let us examine this formulation. Consider the rate equation

$$da/dt = k^\dagger(a - a^*) \qquad (40)$$

This gives

$$k^\dagger = (da/dt)/(a - a^*) \qquad (41)$$

The quantity θ is defined by Weisz and Prater to be

$$\theta = (R^2/D)k^\dagger = (R^2/D)[(da/dt)/(a - a^*)] \qquad (42)$$

and the criterion is

$$\theta = (R^2/D)[(da/dt)/(a - a^*)] \leqslant 1 \qquad (43)$$

For multicomponent systems this criterion needs modification. This may be seen from the following example: In general, during the course of a reaction, the amount a_i may become equal to a_i^* even though the reaction rate da_i/dt is not zero (a_i overshoots the equilibrium value a_i^*). Hence the criterion can become infinite even though there may be no significant diffusion effects whatsoever.

Let us establish a criterion, based on observed *rates* of reaction instead of on observed rate constants, that is more broadly applicable to systems of coupled first order reactions. The transformation that changes the characteristic species, arising from the matrix $\mathbf{D}^{-1}\mathbf{K}^\dagger$, into the molecular species is given by

$$\mathbf{a} = \mathbf{Y}\mathbf{b} = \Sigma_j b_j \mathbf{Y}_j \qquad (44)$$

where $\mathbf{Y}_j$ is the jth characteristic vector which forms the jth column of the transformation matrix $\mathbf{Y}$. Let us define the norm of the vector $\mathbf{a}$ to be

$$|\mathbf{a}| \equiv \sqrt{\mathbf{a}^T(\mathbf{A}^*)^{-1}\mathbf{D}\mathbf{a}} = \sqrt{\Sigma_i D_i a_i^2/a_i^*} \qquad (45)$$

Since

$$\mathbf{Y}_i^T(\mathbf{A}^*)^{-1}\mathbf{D}\mathbf{Y}_j = \delta_{ij} \qquad (46)$$

where δ_{ij} is the Kronecker delta, the norm defined above is the length of the composition vector in the characteristic system of coordinates of the matrix $\mathbf{D}^{-1}\mathbf{K}^\dagger$;

$$|\mathbf{a}| = \sqrt{\Sigma_j b_j^2} \qquad (47)$$

The norm of the vector $[\mathbf{D}^{-1}(d\mathbf{a}/dt)]$ is given by

$$|\mathbf{D}^{-1}(d\mathbf{a}/dt)| = \sqrt{[\mathbf{D}^{-1}(d\mathbf{a}/dt)]^T(\mathbf{A}^*)^{-1}\mathbf{D}[\mathbf{D}^{-1}(d\mathbf{a}/dt)]} \qquad (48)$$

But

$$|\mathbf{D}^{-1}(d\mathbf{a}/dt)| = |\mathbf{D}^{-1}\mathbf{K}^\dagger\mathbf{a}| = |\mathbf{Y}(\boldsymbol{\theta}/R^2)\mathbf{Y}^{-1}\mathbf{a}| = |\mathbf{Y}(\boldsymbol{\theta}/R^2)\mathbf{b}| \qquad (49)$$

since

$$\mathbf{D}^{-1}\mathbf{K}^\dagger = \mathbf{Y}(\boldsymbol{\theta}/R^2)\mathbf{Y}^{-1} \qquad (50)$$

Hence,

$$|\mathbf{D}^{-1}(d\mathbf{a}/dt)| = |\mathbf{Y}(\boldsymbol{\theta}/R^2)\mathbf{b}| = \sqrt{\mathbf{b}^T(\boldsymbol{\theta}/R^2)[\mathbf{Y}^T(\mathbf{A}^*)^{-1}\mathbf{D}\mathbf{Y}](\boldsymbol{\theta}/R^2)\mathbf{b}} \qquad (51)$$

Using the relation

$$\mathbf{Y}^T(\mathbf{A}^*)^{-1}\mathbf{D}\mathbf{Y} = \mathbf{I}$$

the norm becomes

$$|\mathbf{D}^{-1}(d\mathbf{a}/dt)| = \sqrt{\mathbf{b}^T(\boldsymbol{\theta}^2/R^4)\mathbf{b}} = \sqrt{\Sigma_i(b_i\theta_i/R^2)^2} \qquad (52)$$

The inequality

$$\sqrt{\Sigma_i(b_i\theta_i/R^2)^2} \leqslant \sqrt{\Sigma_i(\theta_{\max}b_i/R^2)^2} \leqslant (\theta_{\max}/R^2)\sqrt{\Sigma_i b_i^2} \qquad (53)$$

must hold; hence the relation

$$|\mathbf{D}^{-1}(d\mathbf{a}/dt)| = \sqrt{\frac{\Sigma_i(b_i\theta_i/R^2)^2}{\Sigma_i b_i^2}} \leqslant (\theta_{\max}/R^2) \qquad (54)$$

is obtained. Therefore, by using the definition of the norm given in Eq. (45), the criterion for negligible diffusion effects becomes

$$\theta_{\text{avg}} = R^2\frac{|\mathbf{D}^{-1}(d\mathbf{a}/dt)|}{|\mathbf{a}|} = R^2\sqrt{\frac{\Sigma_i(da_i/dt)^2/D_i a_i^*}{\Sigma_i a_i^2 D_i/a_i^*}} \leqslant 1 \qquad (55)$$

When all diffusivities are equal, it becomes

$$\theta_{\text{avg}} = \frac{R^2}{D}\sqrt{\frac{\Sigma_i(da_i/at)^2/a_i^*}{\Sigma_i a_i^2/a_i^*}} \leqslant 1 \qquad (56)$$

When the amounts, a_i^*, are all equal, it becomes

$$\theta_{\text{avg}} = \frac{R^2}{D}\sqrt{\frac{\Sigma_i(da_i/dt)^2}{\Sigma_i a_i^2}} \leqslant 1 \qquad (57)$$

As an example let us examine the reaction among the species A_1, A_2, and A_3 with the following characteristics: the observed rates are -1×10^{-3} sec^{-1}, 0.5×10^{-3} sec^{-1}, and 0.5×10^{-3} sec^{-1}, respectively; the diffusivities are 2×10^{-3}, 1×10^{-3}, and 1×10^{-3} cm^2/sec, respectively; the equilibrium mole fractions are 0.25, 0.25; and 0.5, respectively; the mole fractions of reactants are 1, 0, and

0, respectively. The criterion given by Eq. (55) becomes

$$\theta_{\text{avg}} = R^2 \cdot \sqrt{\frac{[(1)^2/(2 \times 0.25)] + [(0.5)^2/(1 \times 0.25)] + [(0.5)^2/(1 \times 0.5)]}{2 \times (1)^2/0.25}} = 0.66R^2$$

Thus, if the radius of the sphere is 0.2 cm, $\theta_{\text{avg}} = 0.0264$ and diffusion effects are negligible; but if the radius is 2 cm, $\theta_{\text{avg}} = 2.64$ and diffusion effects are not negligible.

III. The Transient Solution for a Spherical Particle for Equal Diffusivities

Let us assume that the ambient concentrations do not change with time and that the concentrations in the interior of the particle are initially zero. Solutions are then sought for the differential equation

$$\partial/\partial t[\mathbf{a}(r,t)] - \mathbf{D}\nabla^2\mathbf{a}(r,t) + \mathbf{K}\mathbf{a}(r,t) = 0 \quad (58)$$

In general the solution for this equation is not available since one cannot simultaneously diagonalize the matrices **D** and **K**. If all the diffusivities are equal, however, the matrix **D** reduces to a scalar constant and one obtains

$$\partial/\partial t[\mathbf{a}(r,t)] - D\nabla^2\mathbf{a}(r,t) + \mathbf{K}\mathbf{a}(r,t) = 0 \quad (59)$$

The transformations given by Eqs. (6) and (7) are used to convert Eq. (59) into the equation

$$\partial/\partial t[\mathbf{b}(r,t)] - D\nabla^2\mathbf{b}(r,t) + \mathbf{\Lambda}\mathbf{b}(r,t) = 0 \quad (60)$$

Since the matrix $\mathbf{\Lambda}$ is diagonal, Eq. (60) is equivalent to the set of n independent scalar equations of the form

$$\partial/\partial t[b_j(r,t)] - D\nabla^2 b_j(r,t) + \lambda_j b(r,t) = 0 \quad (61)$$

Once again, the highly coupled set of equations given by the matrix Eq. (59) is reduced to a set of simple equations that can be solved individually. Thus, as for the steady state solution, the known solution for a simple irreversible sink involving a single molecular species [Danckwerts (*5*)] may be used for the complex system if the diffusivities of the various molecular species are equal. This solution is

$$b_j(r,t) = b_j^\circ \left\{ \frac{R}{r} \frac{\sinh \varphi_j r/R}{\sinh \varphi_j} + 2 \sum_{n=1} \frac{(-1)^n (n\pi)}{\varphi_j^2 + (n\pi)^2} \frac{\sin (n\pi r/R)}{r} \times \exp - [\varphi_j^2 + (n\pi)^2]\tau \right\} \quad (44)$$

where b_j° is the ambient concentration of the characteristic species B_j and $\tau = Dt/R^2$.

The approach to steady state conditions may be conveniently indexed by the parameter $\xi_j(\varphi_j,\tau)$, which is defined as the total concentration in the sphere divided by the total steady state concentration in the sphere; i.e.,

$$\xi_j(\varphi_j,\tau) \equiv \int_0^R r^2 b_j(r,\tau)dr \Big/ \int_0^R r^2 b_j(r,\infty)dr \quad (63)$$

The value of $\xi_j(r,\tau)$, as determined from Eq. (62), is given by

$$\xi_j(\varphi_j,\tau) = 1 - \frac{6 \sum_{n=1}^{\infty} \exp - [\varphi_j^2 + (n\pi)^2]/[\varphi_j^2 + (n\pi)^2]}{(3/\varphi_j^2)(\varphi_j \coth \varphi_j - 1)} \quad (64)$$

The function $\xi_j(\varphi_j,\tau)$ increases monotonically with φ_j; hence the presence of the chemical reaction will accelerate the approach to the steady state; the characteristic species that is slowest in approaching the steady state is the equilibrium species B_1. Equation (64) is complex and a convenient close approximation for it has been found that is far easier to use. It is

$$\xi_j(\varphi_j,\tau) \cong \text{erf}\sqrt{(7.5 + \varphi_j^2)\tau} = \text{erf}\sqrt{7.5\tau + \lambda_j t} \quad (65)$$

A comparison of this approximation with the correct equation is given in Table 1. According to Eq. (65) the total concentration within the spherical particle will have reached 95% of the total steady state concentration when

$$\tau = (1.386)^2/(7.5 + \varphi^2) \quad (66)$$

Hence,

$$(7.5 + \varphi^2)\tau \geqslant 2$$

may be taken as a convenient criterion for the disappearance of significant transient effects.

TABLE 1

THE TRANSIENCE FACTOR ξ AS A FUNCTION OF φ AND τ IN COMPARISON WITH THE APPROXIMATION FORMULA

φ	τ	ξ	erf $\sqrt{(7.5 + \varphi)\tau}$
0	.0001	.0336	0.310
	.001	.104	.097
	.01	.309	.302
	.1	.772	.779
	1.0	.99997	.99989
1	.0001	.0358	.0329
	.001	.1109	.1038
	.01	.3288	.3204
	.1	.7987	.8082
	.2	.9330	.9344
5	.0001	.070	.0644
	.001	.2169	.2009
	.01	.5954	.5798
	.02	.7550	.7463
	.1	.9888	.9893
10	.0001	.1240	.1166
	.001	.3729	.3552
	.01	.8661	.8575
	.02	.9644	.9619
20	.00001	.0748	.0712
	.0001	.2324	.2249
	.001	.6443	.6331
	.01	.9960	.9957
50	.000001	.0575	.0564
	.00001	.1806	.1768
	.0001	.5266	.5205
	.0003	.7844	.7798
	.001	.9758	.9747
100	.000001	.1137	.1125
	.00001	.3498	.3451
	.0001	.8448	.8427
	.0003	.9859	.9856

IV. DISCUSSION AND SUMMARY

The solution for the effect of intraparticle diffusion on the behavior of complex systems of first order reactions has been obtained, using the matrix $\mathbf{Y}$, by transforming the system of molecular species into a system of characteristic species or "transference units." This transformation has the effect of changing the highly coupled system of diffusion equations for the molecular species into a set of uncoupled, and therefore independent, diffusion equations for the characteristic species. The required transformation can be determined from experimental data, since matrix $\mathbf{Y}$ is formed from the characteristic vectors of the matrix $\mathbf{D}^{-1}\mathbf{K}^{\dagger}$. For systems studied in the laboratory, the matrix $\mathbf{K}^{\dagger}$ is determined from the equilibrium composition and the location of the straight line reaction paths (which constitutes the matrix $\mathbf{X}^{\dagger}$), and the rate of reaction of each characteristic species (which constitutes the matrix $\mathbf{\Lambda}^{\dagger}$) [Wei and Prater (*6*)]. The characteristic vectors of the matrix $\mathbf{D}^{-1}\mathbf{K}^{\dagger}$ may then be computed [Wei and Prater (*6*)] using the measured values of the diffusivities [Weisz (*10*)]. However, if the diffusivities are equal, the matrix $\mathbf{Y}$ is identical to the matrix $\mathbf{X}^{\dagger}$; this greatly simplifies the computations.

In part II of this paper, the method of analysis and the results obtained for a single particle will be applied to packed bed and stirred tank reactors. The study of these reactors is best made in terms of the straight line reaction paths, and consequently the rate constant matrix $\mathbf{K}^{\dagger}$ may be obtained rather easily. The question then arises as to whether or not the rate-constant matrix obtained is a diffusion-disguised rate-constant matrix. This may be determined by computing an upper limit for the maximum value of the characteristic value θ_n/R^2 of the matrix $\mathbf{D}^{-1}\mathbf{K}^{\dagger}$.

When the diffusivities of the various reactants are equal in value, the treatment of the systems for the steady state condition is greatly simplified, and the solution for the transient condition is obtained for systems of arbitrary complexity. The assumption of equal diffusivities is a good approximation for a large fraction of cases of interest since the diffusivity generally varies inversely as the square root of the molecular weight, and most first order or pseudo-first-order systems do not produce large changes in molecular weight except in reaction steps for which irreversibility is a good approximation. Hence, except for sieve catalyst particles in which the diffusivity of highly branched molecules may be sterically hindered and essentially reduced to zero, the solution obtained for equal diffusivity is, in most cases, a good approximation for the actual behavior of coupled systems of first order reactions. These solutions are certainly useful for estimating the importance of diffusion effects in such reaction systems.

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