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On a Tracer Method for Evaluating Catalytic Data

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This paper presents theoretical studies of a method of using a radioactive tracer technique to evaluate the kinetic data of heterogeneous catalytic reactions that are coupled with a Knudsen type of pore diffusion. By superimposing a transient radioactive tracer response over the steady state concentration profile in the catalyst particle, one can establish an implicit relation between the total amount of radioactive components diffused out of the particle and the kinetic data of the reaction system. This relation can then be used to evaluate kinetic data of the reaction system. A detailed study of general monomolecular complex systems is given. Use of the method for nonlinear systems is also included.

In 1939 Thiele (*1*) pointed out that the performance of a simple catalytic reaction may be well described by a single dimensionless parameter. Now well known as the Thiele modulus, it is composed of the kinetic rate constant, effective diffusivity of the reactant in the pore of the catalyst, size of the catalyst particle (or size of the pore), and the external concentration of the reactant (for reactions other than first order). In recent years, this modulus has been a major target of the intensive research to determine catalyst activity and the kinetics of the chemical reaction system. To evaluate this modulus, it is necessary to determine both the kinetic rate constant and the effective diffusivity of the reactant in the pore of the catalyst. There are many methods available for this purpose (*2* to *7*).

Recently Brinkley and Peterson (*8*) proposed a new method for measuring the Thiele modulus of a first-order isothermal irreversible catalytic reaction. Basically, their idea was to add a small quantity of radioactively tagged molecules in the reactant stream, which is allowed to reach steady state in the catalytic particle. The tagged reactant stream is then suddenly replaced by a pure nonradioactive reactant stream without affecting the steady state profile of the total (radioactive plus nonradioactive) reactant in the particle. One may then collect the total effluent stream after the tagged reactant stream has been replaced by a nonradioactive reactant stream and measure the ratio of the total amount of radioactive product to radioactive reactant in the collected sample. A functional relation between this ratio and the Thiele modulus is established upon theoretical grounds, and the Thiele modulus can then be evaluated. Brinkley and Peterson also proposed a set of experimental designs for a differential reactor and a sampling device. The advantage of using a differential reactor is that one does not have to worry about the axial diffusion in the bulk fluid, so an analysis for a single catalyst particle is sufficient for obtaining the functional relation.

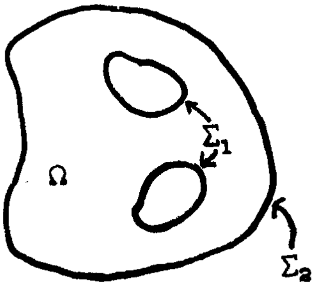
If one uses the technique for more complicated reaction systems other than the first-order irreversible reaction system, one can use product distribution as well as the isotopic distribution as a double check. There are, however, some possible experimental difficulties. The generation of the step function at the particle boundary is difficult because the radioactive materials in the boundary layer around the catalyst particle will not disappear right away. Furthermore, the method uses a transient effective diffusivity, which may be different from a steady state effective diffusivity if the amount of adsorption on the active surface of the catalyst is extensive and the rate of desorption is slow. It may be that the steady state effective diffusivity is more relevant to the Thiele modulus. The duration of the transience is likely to be short. For a ¼ in. diameter sphere of $D = 10^{-3}$ sq.cm./sec., 92% of the radioactive materials would have left the sphere in 20 sec. Except for these limitations, the proposal of Brinkley and Peterson is an excellent one. Unfortunately, for a single first-order irreversible reaction in a catalyst pore of cylindrical shape, their mathematical treatment contains some unnecessary mathematical assumptions, and, consequently, their result is mathematically not exact. A comparison between their results and ours will be given later in this paper.

In this paper, an exact mathematical treatment of the method is given for a general monomolecular complex reaction system. (A more general type of boundary condition is used.) The fundamental relation between the total amounts of each radioactive species in the effluent stream and the reaction-constant matrix may be expressed either in a vector or a matrix form. It should be noted that our present treatment is completely independent of Brinkley and Peterson's treatment and contains no mathematical approximation.

The present treatment is also extended to include nonlinear systems, which are illustrated by treating the problem of a single nonisothermal reaction with general kinetics in a catalytic particle of a general shape.

THE GENERAL MONOMOLECULAR REACTION SYSTEM

Let us consider a single catalyst particle with closed region Ω as the interior of the particle and orientable and closed $\Sigma \equiv \Sigma_1 + \Sigma_2$ as the surface of the particle.



Then the steady state equation for an isothermal monomolecular reaction system may be written in vector and matrix form as

$$\mathbf{D}\nabla^2 \mathbf{c}_s - \mathbf{K}\mathbf{c}_s = \mathbf{o} \qquad \mathbf{r}\epsilon\Omega \qquad (1)$$

where $\mathbf{c}_s(\mathbf{r})$ is the N dimensional steady state concentration vector $[c_s^{(1)}, c_s^{(2)}, \ldots, c_s^{(N)}]^T$, and $\mathbf{D}$ and $\mathbf{K}$ are the diffusion and reaction rate constant matrices. If the surface Σ_1 is nonexistent or inaccessible to mass transfer, the boundary conditions are

$$\mathbf{D}(\mathbf{n}\cdot\nabla)\mathbf{c}_s = \mathbf{o} \qquad \mathbf{r}\epsilon\Sigma_1 \qquad (1a)$$

and

$$\mathbf{D}(\mathbf{n}\cdot\nabla)\mathbf{c}_s = -\mathbf{H}(\mathbf{c}_s - \mathbf{c}_e) \qquad \mathbf{r}\epsilon\Sigma_2 \qquad (1b)$$

(When Σ_1 is accessible to mass transfer, the analysis can only be done for the particle with symmetric geometry in which the mass transfer depends on a single scalar position variable, such as a hollow sphere.) Since $\mathbf{D}$ is in general nonsingular, Equation (1), with conditions (1*a*) and (1*b*), may be converted to

$$\nabla^2\mathbf{c}_s - L^{-2}\,\underset{\sim}{\Phi}^2\mathbf{c}_s = \mathbf{o} \qquad \mathbf{r}\epsilon\Omega \qquad (2)$$

$$(\mathbf{n}\cdot\nabla)\mathbf{c}_s = \mathbf{o} \qquad \mathbf{r}\epsilon\Sigma_1 \qquad (2a)$$

and

$$(\mathbf{n}\cdot\nabla)\mathbf{c}_s = -L^{-1}\mathbf{N}_{Nu}(\mathbf{c}_s - \mathbf{c}_e) \qquad \mathbf{r}\epsilon\Sigma_2 \qquad (2b)$$

where $\underset{\sim}{\Phi} = L(\mathbf{D}^{-1}\mathbf{K})^{1/2}$, $\mathbf{N}_{Nu} = L\mathbf{D}^{-1}\mathbf{H}$, and L is the characteristic length of the particle. We observe that the dimensionless matrix $\underset{\sim}{\Phi}$ plays a similar role for a complex reaction system as the Thiele modulus does for a system of a single reaction.

In the following analysis we assume that the mass transfer Nusselt numbers of all species are all equal; that is, $\mathbf{N}_{Nu} = N_{Nu}\mathbf{I}$, and therefore the boundary condition (2*b*) becomes

$$(\mathbf{n}\cdot\nabla)\mathbf{c}_s = -\frac{N_{Nu}}{L}(\mathbf{c}_s - \mathbf{c}_e) \qquad \mathbf{r}\epsilon\Sigma_2 \qquad (2c)$$

The solution of Equation (2) with conditions (2*a*) and (2*c*) may be given in the following form:

$$\mathbf{c}_s(\mathbf{r}) = \mathbf{M}(\underset{\sim}{\Phi}, \mathbf{r}/L, N_{Nu})\mathbf{c}_e \qquad (3)$$

where $\mathbf{M}(\underset{\sim}{\Phi}, \mathbf{r}/L, N_{Nu})$ satisfies the differential equation

$$\nabla^2\mathbf{M} - L^{-2}\,\underset{\sim}{\Phi}^2\mathbf{M} = \mathbf{0} \qquad \mathbf{r}\epsilon\Omega \qquad (4)$$

with boundary conditions

$$(\mathbf{n}\cdot\nabla)\mathbf{M} = \mathbf{0} \qquad \mathbf{r}\epsilon\Sigma_1 \qquad (4a)$$

and

$$(\mathbf{n}\cdot\nabla)\mathbf{M} = -\frac{N_{Nu}}{L}(\mathbf{M} - \mathbf{I}) \qquad \mathbf{r}\epsilon\Sigma_2 \qquad (4b)$$

Let $\underset{\sim}{\alpha}$ be the radioactive tracer concentration vector corresponding to $\mathbf{c}_s$ with the initial condition

$$\underset{\sim}{\alpha} = \mu\mathbf{c}_s \quad t = 0, \quad \mathbf{r}\epsilon\Omega + \Sigma_1 + \Sigma_2 \qquad (5a)$$

where μ is the fraction of tagged molecules in the initial feed. The transient equation for $\underset{\sim}{\alpha}$ is

$$\frac{\partial\underset{\sim}{\alpha}}{\partial t} = \mathbf{D}\nabla^2\underset{\sim}{\alpha} - \mathbf{K}\underset{\sim}{\alpha} \quad t > 0, \ \mathbf{r}\epsilon\Omega \qquad (5)$$

with boundary conditions

$$(\mathbf{n}\cdot\nabla)\underset{\sim}{\alpha} = \mathbf{o} \quad t > 0, \ \mathbf{r}\epsilon\Sigma_1 \qquad (5b)$$

and

$$(\mathbf{n}\cdot\nabla)\underset{\sim}{\alpha} = -\frac{N_{Nu}}{L}\underset{\sim}{\alpha} \quad t > 0, \ \mathbf{r}\epsilon\Sigma_2 \qquad (5c)$$

In addition to conditions (5*a*), (5*b*), and (5*c*), we expect that

$$\underset{\sim}{\alpha} \to \mathbf{o} \quad \text{as } t \to \infty, \ \mathbf{r}\epsilon\Omega + \Sigma_1 + \Sigma_2 \qquad (5d)$$

If we now assume that $\int_0^\infty \underset{\sim}{\alpha}(\mathbf{r}, t)dt$ exists for all $\mathbf{r}\epsilon\Omega + \Sigma_1 + \Sigma_2$ and let

$$\underset{\sim}{\beta}(\mathbf{r}) \equiv \int_0^\infty \underset{\sim}{\alpha}(\mathbf{r}, t)dt \qquad (6)$$

we may integrate Equation (5) and conditions (5*b*) and (5*c*) with respect to t from $t = 0$ to $t = \infty$ and obtain

$$\int_0^\infty \frac{\partial\underset{\sim}{\alpha}}{\partial t}dt = -\mu\mathbf{c}_s = \mathbf{D}\nabla^2\underset{\sim}{\beta} - \mathbf{K}\underset{\sim}{\beta} \quad \mathbf{r}\epsilon\Omega \qquad (7)$$

$$(\mathbf{n}\cdot\nabla)\underset{\sim}{\beta} = \mathbf{o} \qquad \mathbf{r}\epsilon\Sigma_1 \qquad (7a)$$

and

$$(\mathbf{n}\cdot\nabla)\underset{\sim}{\beta} = -\frac{N_{Nu}}{L}\underset{\sim}{\beta} \qquad \mathbf{r}\epsilon\Sigma_2 \qquad (7b)$$

In deriving Equation (7), we have assumed that $\int_0^\infty \nabla^2\underset{\sim}{\alpha}dt = \nabla^2\int_0^\infty \underset{\sim}{\alpha}dt$ (see reference 9 for the conditions on $\underset{\sim}{\alpha}$ to make this manipulation legitimate). Equation (7) may be further converted to the following form:

$$-\mu\mathbf{D}^{-1}\,\mathbf{M}\mathbf{c}_e = \nabla^2\underset{\sim}{\beta} - L^{-2}\,\underset{\sim}{\Phi}^2\underset{\sim}{\beta} \qquad \mathbf{r}\epsilon\Omega \qquad (8)$$

If we now multiply Equation (8) from the left by **M** and then integrate the resulting equation with respect to **r** over Ω, we obtain

$$\begin{aligned}
-\mu\textstyle\int_\Omega \mathbf{M}\mathbf{D}^{-1}\,\mathbf{M}dV\ \ \mathbf{c}_e &= \textstyle\int_\Omega \mathbf{M}\nabla^2\underset{\sim}{\beta}dV - L^{-2}\textstyle\int_\Omega \mathbf{M}\underset{\sim}{\Phi}^2\underset{\sim}{\beta}dV \\
&= \textstyle\int_\Omega \nabla\cdot(\mathbf{M}\nabla\underset{\sim}{\beta})dV - \textstyle\int_\Omega(\nabla\mathbf{M})\cdot(\nabla\underset{\sim}{\beta})dV \\
&\qquad - L^{-2}\underset{\sim}{\Phi}^2\textstyle\int_\Omega \mathbf{M}\underset{\sim}{\beta}dV \\
&= \textstyle\int_{\Sigma_1+\Sigma_2}\mathbf{M}(\mathbf{n}\cdot\nabla)\underset{\sim}{\beta}dS - \textstyle\int_\Omega(\nabla\mathbf{M})\cdot(\nabla\underset{\sim}{\beta})dV \\
&\qquad - L^{-2}\underset{\sim}{\Phi}^2\textstyle\int_\Omega \mathbf{M}\underset{\sim}{\beta}dV \\
&\qquad \text{(from the divergence theorem)} \qquad (9) \\
&= \textstyle\int_{\Sigma_2}\mathbf{M}(\mathbf{n}\cdot\nabla)\underset{\sim}{\beta}dS - \textstyle\int_\Omega(\nabla\mathbf{M})\cdot(\nabla\underset{\sim}{\beta})dV \\
&\qquad - L^{-2}\underset{\sim}{\Phi}^2\textstyle\int_\Omega \mathbf{M}\underset{\sim}{\beta}dV \\
&\qquad \text{[from boundary condition (7}a\text{)]}
\end{aligned}$$

The manipulations here are legitimate, since **M** is a function of $\underset{\sim}{\Phi}$ so that $\underset{\sim}{\Phi}^2\mathbf{M} = \mathbf{M}\underset{\sim}{\Phi}^2$. If we multiply $\underset{\sim}{\beta}$ by Equation (4) and then integrate the resulting equation with respect to **r** over Ω, we obtain

$$-\frac{N_{Nu}}{L}\textstyle\int_{\Sigma_2}(\mathbf{M}-\mathbf{I})\underset{\sim}{\beta}dS - \textstyle\int_\Omega(\nabla\mathbf{M})\cdot(\nabla\underset{\sim}{\beta})dV - L^{-2}\,\underset{\sim}{\Phi}^2\textstyle\int_\Omega \mathbf{M}\underset{\sim}{\beta}dV = \mathbf{o} \qquad (10)$$

after using the divergence theorem and conditions (4*a*) and (4*b*). After (7*b*) is used, this equation may further be converted to

$$\textstyle\int_{\Sigma_2}(\mathbf{M}-\mathbf{I})(\mathbf{n}\cdot\nabla)\underset{\sim}{\beta}dS - \textstyle\int_\Omega(\nabla\mathbf{M})\cdot(\nabla\underset{\sim}{\beta})dV - L^{-2}\,\underset{\sim}{\Phi}^2\textstyle\int_\Sigma \mathbf{M}\underset{\sim}{\beta}dV = \mathbf{o} \qquad (11)$$

Combining Equations (9) and (11), we finally obtain

$$\mathbf{a} \equiv -\mathbf{D}\textstyle\int_{\Sigma_2}(\mathbf{n}\cdot\nabla)\underset{\sim}{\beta}dS = \mu\mathbf{D}\textstyle\int_\Omega \mathbf{M}\mathbf{D}^{-1}\,\mathbf{M}dV\ \ \mathbf{c}_e \quad (12)$$

where $\mathbf{a} \equiv -\int_o^\infty\int_{\Sigma_2}\mathbf{D}(\underset{\sim}{\mathbf{n}}\cdot\nabla)\underset{\sim}{\alpha}dSdt$ is a vector whose i^{th} element represents the total amount of the i^{th} radioactive tracer component in the collected effluent sample. Since **a** is measurable, Equation (12) is an implicit function of $L^2\mathbf{D}^{-1}\mathbf{K}$ and $\mathbf{D}^{-1}$ and may be used to evaluate **K** if **D** is either known or measurable.

A well-designed set of experiments will enable us to transform Equation (12) into a neater form; it is done by running N experiments with N independent $\mathbf{c}_e$, say $\mathbf{c}_e^{(i)}$ ($i = 1, 2, \ldots, N$) (with other conditions remaining the same). For convenience, let us call the corresponding vectors at the left-hand side of Equation (12) $\mathbf{a}^{(i)}$ ($i = 1, 2, \ldots, N$). The total experimental result may be given as

$$\mathbf{D}\int_\Omega \mathbf{M}\mathbf{D}^{-1}\,\mathbf{M}dV\ \ \mathbf{C}_e = \frac{1}{\mu}\mathbf{A}$$

or (13*a*)

$$\mathbf{D}\int_\Omega \mathbf{M}\mathbf{D}^{-1}\,\mathbf{M}dV = \frac{1}{\mu}\mathbf{A}\mathbf{C}_e{}^{-1}$$

where $\mathbf{C}_e = [\mathbf{c}_e^{(1)}, \ldots, \mathbf{c}_e^{(N)}]$ and $\mathbf{A} = [\mathbf{a}^{(1)}, \ldots, \mathbf{a}^{(N)}]$. Expression (13*a*) may be further simplified if we set the elements of $\mathbf{c}_e^{(i)}$ to be zero except the i^{th} one which equals c_e; in other words, each experiment has a feed of pure component i. The expression becomes

$$\mathbf{D}\int_\Omega \mathbf{M}\mathbf{D}^{-1}\,\mathbf{M}dV = \frac{1}{\mu c_e}\mathbf{A} \qquad (13b)$$

For general monomolecular reaction systems, an explicit expression for the integral $\int_\Omega \mathbf{M}\mathbf{D}^{-1}\,\mathbf{M}dV$ is very difficult to give. In the following two sections we shall give some more explicit results for two simpler cases: a monomolecular reaction system with equal diffusivities, and a general two-component system.

MONOMOLECULAR REACTION SYSTEM WITH EQUAL DIFFUSIVITIES

For a system with equal diffusivities, Equations (12) and (13*b*) may be simplified to

$$\int_\Omega [\mathbf{M}(L^2D^{-1}\mathbf{K}, \mathbf{r}/L, N_{Nu}]^2\,dV\ \ \mathbf{c}_e = -\frac{D}{\mu}\int_{\Sigma_2}(\mathbf{n}\cdot\nabla)\underset{\sim}{\beta}dS \qquad (14)$$

and

$$\int_\Omega \mathbf{M}^2\,dV = \frac{1}{\mu c_e}\mathbf{A} \qquad (15)$$

There exists a matrix **X** (*10*) composed of the eigenvectors of **K** such that $\mathbf{X}^{-1}\mathbf{K}\mathbf{X}$ becomes a diagonal matrix with real non-negative diagonal elements. The same similarity transformation will transform $\mathbf{M}^2$ into its corresponding diagonal form because **M** is a function of **K**. Consequently, the integral $\int_\Omega \mathbf{M}^2dV$ may be performed by transforming $\mathbf{M}^2$ into its diagonal form, by integrating the diagonal form, and finally by transforming the result back to its original system. To illustrate further analysis, we assume the particle has the geometry of a sphere with no Σ_1.
Let

$$\underset{\sim}{\Lambda} = \mathbf{X}^{-1}\,\underset{\sim}{\Phi}\mathbf{X} \qquad (16)$$

where $\underset{\sim}{\Lambda}$ is a diagonal matrix with λ_i, $i = 1, 2, \ldots, N$ as its diagonal elements and $\lambda_1 = 0$, $\lambda_i > 0$ ($i = 2, 3, \ldots, N$). The steady state solution for a spherical particle is

$$\mathbf{c}_s = \mathbf{X}\,[\underset{\sim}{\Lambda}\cosh\underset{\sim}{\Lambda} + (N_{Nu}-1)\sinh\underset{\sim}{\Lambda}]^{-1}\,\frac{N_{Nu}L}{r}\left(\sinh\underset{\sim}{\Lambda}\frac{r}{L}\right)\mathbf{X}^{-1}\mathbf{c}_e \qquad (17)$$

where L is the radius of the sphere and r is the coordinate of the spherical geometry. Therefore

$$\mathbf{X}^{-1}\,\mathbf{M}\mathbf{X} = [\underset{\sim}{\Lambda}\cosh\underset{\sim}{\Lambda} + (N_{Nu}-1)\sinh\underset{\sim}{\Lambda}]^{-1}\,\frac{N_{Nu}L}{r}\sinh\underset{\sim}{\Lambda}\frac{r}{L} \qquad (18)$$

Note that since $\lambda_1 = 0$, the matrix $\underset{\sim}{\Lambda}\cosh\underset{\sim}{\Lambda} + (N_{Nu}-1)\sinh\underset{\sim}{\Lambda}$ is singular; however, it may be easily shown that the matrix $[\underset{\sim}{\Lambda}\cosh\underset{\sim}{\Lambda} + (N_{Nu}-1)\sinh\underset{\sim}{\Lambda}]^{-1}\sinh\underset{\sim}{\Lambda}\frac{r}{L}$ does indeed exist by taking the limit as $\lambda_1 \rightarrow 0$ and by using de l'Hospital's rule. A similar argument is applied to the following integral:

$$\mathbf{P} \equiv \frac{1}{2\pi L^3}\mathbf{X}^{-1}\int_\Omega \mathbf{M}^2\,dV\,\mathbf{X} = N_{Nu}^2\,\underset{\sim}{\Lambda}^{-1}[\underset{\sim}{\Lambda} + (N_{Nu}-1)\tanh\underset{\sim}{\Lambda}]^{-2}(\tanh\underset{\sim}{\Lambda} - \underset{\sim}{\Lambda}\operatorname{sech}^2\underset{\sim}{\Lambda}) \qquad (19)$$

Combining Equations (15) and (19), we get

$$N_{Nu}^{2}\,\mathbf{X}\underset{\sim}{\Lambda}^{-1}\,[\underset{\sim}{\Lambda} + (N_{Nu} - 1)\tanh\underset{\sim}{\Lambda}]^{-2}(\tanh\underset{\sim}{\Lambda} - \underset{\sim}{\Lambda}\,\mathrm{sech}^2\,\underset{\sim}{\Lambda}]\mathbf{X}^{-1} = (2\pi L^3 \mu c_e)^{-1}\,\mathbf{A} \quad (20)$$

which may be solved for $\underset{\sim}{\Lambda}$ by certain iterative schemes. Note that when the boundary condition is of the Dirichlet type, $N_{Nu} \rightarrow \infty$ and Equation (20) reduces to

$$\mathbf{X}\underset{\sim}{\Lambda}^{-1}\,(\tanh\underset{\sim}{\Lambda})^{-2}\,(\tanh\underset{\sim}{\Lambda} - \underset{\sim}{\Lambda}\,\mathrm{sech}^2\,\underset{\sim}{\Lambda})\mathbf{X}^{-1} = (2\pi L^3 \mu c_e)^{-1}\,\mathbf{A} \quad (21)$$

The diagonal matrix $\underset{\sim}{\Lambda}$ is here equivalent to the Thiele modulus of a single reaction system. Consequently, it may be expected that when chemical reactions are sufficiently fast, when effective diffusivities are sufficiently small, or when the catalyst particle is sufficiently large, λ_i, $i = 2, 3, \ldots, N$, becomes large and Equations (20) and (21) may be written in asymptotic forms. Since $\tanh \lambda_i \sim 1.0$ and $\mathrm{sech}^2\,\lambda_i \sim 0.0$ within 1% error for $\lambda_i > 3.0$, we have

$$(\mathbf{P})_1 = \frac{2}{3}$$

and (22)

$$(\mathbf{P})_i = N_{Nu}^{2}\,\lambda_i^{-1}\,(\lambda_i + N_{Nu} - 1)^{-2} \text{ for } \lambda_i > 3.0, \quad i = 2, 3, \ldots, N$$

where $(\mathbf{P})_i$ = i^{th} diagonal element of $\mathbf{P}$, $(i = 1, 2, \ldots, N)$. Therefore

$$\mathbf{P}^{-1} = N_{Nu}^{-2}\,\underset{\sim}{\Lambda}\,[\underset{\sim}{\Lambda} + (N_{Nu} - 1)\,\mathbf{I}]^2 + \frac{3}{2}\,\mathbf{E}_{11} \quad (23)$$

where $\mathbf{E}_{11}$ is a matrix with zero elements everywhere except in its first diagonal element, which is unity. After using Equations (23), (15), and (19) we obtain for $\lambda_i > 3.0$ $(i = 2, 3, \ldots, N)$

$$N_{Nu}^{-2}\,\mathbf{X}\underset{\sim}{\Lambda}\,[\underset{\sim}{\Lambda} + (N_{Nu} - 1)\,\mathbf{I}]^2\mathbf{X}^{-1} + \frac{3}{2}\,\mathbf{X}\mathbf{E}_{11}\mathbf{X}^{-1} = 2\pi L^3\,\mu c_e\mathbf{A}^{-1}$$

or (24)

$$N_{Nu}^{-2}\,\underset{\sim}{\Phi}\,[\underset{\sim}{\Phi} + (N_{Nu} - 1)\,\mathbf{I}]^2 = 2\pi L^3\,\mu c_e\mathbf{A}^{-1} - \frac{3}{2}\,\mathbf{X}\mathbf{E}_{11}\,\mathbf{X}^{-1}$$

However, it is known that $\mathbf{X}$ can be constructed in such a way that its first column is simply the equilibrium composition vector of the reaction system, and the elements of the first row of $\mathbf{X}^{-1}$ are all unity [see *(10)*]. Therefore

$$\mathbf{X}\mathbf{E}_{11}\mathbf{X}^{-1} = \mathbf{c}^{*}\mathbf{1}^T \quad (25)$$

where $\mathbf{c}^{*}$ is the equilibrium concentration vector of the reaction system and $\mathbf{1}$ is the vector with unity elements. Since $\mathbf{c}^{*}$ may be accurately determined either experimentally or by the use of thermodynamical properties of the existing chemical species, we may assume it is known. Combining Equations (24) and (25), we obtain

$$N_{Nu}^{-2}\,\underset{\sim}{\Phi}\,[\underset{\sim}{\Phi} + (N_{Nu} - 1)\,\mathbf{I}]^2 = 2\pi L^3\,\mu c_e\mathbf{A}^{-1} - \frac{3}{2}\,\mathbf{c}^{*}\mathbf{1}^T \quad (26)$$

which may be easily solved for $\underset{\sim}{\Phi}$ by some simple iterative processes. When we have a Dirichlet boundary condition, Equation (26) can be further simplified to

$$\underset{\sim}{\Phi} = 2\pi L^3\,\mu c_e\mathbf{A}^{-1} - \frac{3}{2}\,\mathbf{c}^{*}\mathbf{1}^T$$

or (27)

$$\mathbf{K} = \frac{D}{L^2}\left(2\pi L^3\,\mu c_e\mathbf{A}^{-1} - \frac{3}{2}\,\mathbf{c}^{*}\mathbf{1}^T\right)^2$$

Therefore, $\mathbf{K}$ may be easily computed by measuring $\mathbf{A}$.

THE TWO-COMPONENT SYSTEM

In this section we illustrate a method of evaluating the integral $\int_\Omega \mathbf{M}\mathbf{D}^{-1}\mathbf{M}dV$ with $\mathbf{D} \neq D\mathbf{I}$. For this purpose we assume the particle has the geometry of a slab with no Σ_1 (or we consider a system with a long cylindrical pore in a catalyst particle with negligible radial concentration gradient in the pore). The steady state is given as

$$\mathbf{c}_s = N_{Nu}\cosh\underset{\sim}{\Phi}\frac{x}{L}\,(\underset{\sim}{\Phi}\sinh\underset{\sim}{\Phi} + N_{Nu}\cosh\underset{\sim}{\Phi})^{-1}\,\mathbf{c}_e \quad (28)$$

where L is the half-thickness of the slab and x is the coordinate of the slab geometry with $x = 0$ as the center of the slab and $x = L$ as the boundary of the slab. Therefore

$$\mathbf{M} = N_{Nu}\cosh\underset{\sim}{\Phi}\frac{x}{L}\,(\underset{\sim}{\Phi}\sinh\underset{\sim}{\Phi} + N_{Nu}\cosh\underset{\sim}{\Phi})^{-1} \quad (29)$$

Now, there exists a matrix $\mathbf{Y}$ *(11)* composed of the eigenvectors of $\mathbf{D}^{-1}\mathbf{K}$ such that $\mathbf{Y}^{-1}\mathbf{D}^{-1}\mathbf{K}\mathbf{Y}$ becomes a diagonal matrix with real non-negative diagonal elements. For simplicity, we let

$$\underset{\sim}{\Lambda} = \mathbf{Y}^{-1}\,\underset{\sim}{\Phi}\mathbf{Y} \quad (30)$$

Then, obviously

$$\mathbf{Y}^{-1}\,\mathbf{M}\mathbf{Y} = N_{Nu}\cosh\underset{\sim}{\Lambda}\frac{x}{L}\,(\underset{\sim}{\Lambda}\sinh\underset{\sim}{\Lambda} + N_{Nu}\cosh\underset{\sim}{\Lambda})^{-1} \quad (31)$$

For two-component systems, we may let

$$q_1 = L\,(k_1^2/D_1)^{1/2} \qquad q_2 = L\,(k_2^1/D_2)^{1/2}$$
$$R_0 = D_2/D_1 \qquad R_c = c_{e2}/c_{e1}$$

and have

$$L^2\mathbf{D}^{-1}\mathbf{K} = \begin{bmatrix} q_1^2 & -q_2^2R_0 \\ -q_1^2R_0^{-1} & q_2^2 \end{bmatrix}$$

$$\lambda_1 = 0 \quad \lambda_2 = (q_1^2 + q_2^2)^{1/2} \quad (32)$$

$$\mathbf{Y} = \begin{bmatrix} 1 & 1 \\ \dfrac{q_1^2}{q_2^2\,R_0} & -\dfrac{1}{R_0} \end{bmatrix} \qquad \mathbf{Y}^{-1} = \frac{1}{\lambda_2^2}\begin{bmatrix} q_2^2 & q_2^2\,R_0 \\ q_1^2 & -q_2^2\,R_0 \end{bmatrix}$$

By using Equations (31) and (32), it can easily be shown that

$\int_\Omega \mathbf{Y}^{-1}\,\mathbf{M}\mathbf{D}^{-1}\,\mathbf{M}\mathbf{Y}dV =$

$$\frac{SL}{2D_2\,\lambda_2^3}\begin{bmatrix} 2(q_1^2 + R_0\,q_2^2)\,\lambda_2 & 2Gq_2^2\,(R_0 - 1)\,N_{Nu} \\ 2Gq_1^2\,(R_0 - 1)N_{Nu} & G^2\,(R_0\,q_1^2 + q_2^2)\,N_{Nu}^2(\coth\lambda_2 + \lambda_2\,\mathrm{csch}^2\,\lambda_2) \end{bmatrix} \quad (33)$$

where S is the surface area of the boundary $x = L$

$$G = (\lambda_2 + N_{Nu} \coth \lambda_2)^{-1}$$

Therefore, by using **Y** and $\mathbf{Y}^{-1}$ of Equation (32) and performing some tedious manipulations, we obtain

$$\mathbf{D} \int_\Omega \mathbf{M}\mathbf{D}^{-1} \mathbf{M} dV \, \mathbf{c}_e = \frac{SLc_{e_1} G}{2\lambda_2^5 R_0} \begin{bmatrix} 2q_2^2 F_1 + F_2 \\ \\ 2q_1^2 F_1 - F_2 \end{bmatrix} \quad (34)$$

where

$$F_1 = (q_1^2 + R_0 q_2^2)(1 + R_0 R_c) \lambda_2 G^{-1} + (q_1^2 - R_0 R_c q_2^2)(R_0 - 1) N_{Nu} \quad (35)$$

$$F_2 = 2q_1^2 q_2^2 (R_0 - 1)(1 + R_0 R_c) N_{Nu} + (q_1^2 - R_0 R_c q_2^2)(R_0 q_1^2 + q_2^2) N_{Nu}^2 (\coth \lambda_2 + \lambda_2 \operatorname{csch}^2 \lambda_2) G$$

We need only measure the ratio of the total amount of radioactive product to the total amount of radioactive reactant in the effluent sample. This ratio is given as

$$f = \frac{-D_2 \int_{\Sigma_2} (\mathbf{n}\cdot\nabla)\beta_2 \, dS}{-D_1 \int_{\Sigma_2} (\mathbf{n}\cdot\nabla)\beta_1 \, dS} = \frac{2q_1^2 F_1 - F_2}{2q_2^2 F_1 + F_2} \quad (36)$$

Since R_0 may be estimated from the molecular weights of the reactant and the product (for Knudsen diffusivities) or by some other methods (for effective diffusivities), and since k_2^1/k_1^2 the equilibrium constant, may be estimated either experimentally or by using the thermodynamic properties of reactant and product, the right-hand side of Equation (36) is a functional of either q_1 or q_2. Therefore, by measuring the left-hand side of Equation (36), q_1 or q_2 may then be computed.

Equation (36) may be somewhat simplified for some simpler cases, such as $N_{Nu} \to \infty$ or $q_2 = 0$ or $R_0 = 1$ or $R_c = 0$ etc. The simplest case is the one with $N_{Nu} \to \infty$, $q_2 = 0$, $R_0 = 1$, and $R_c = 0$, which is the same system presented by Brinkley and Peterson (8). For this case, Equation (36) is reduced to

$$f = 2\left(\frac{\tanh q_1}{q_1} + \operatorname{sech}^2 q_1\right)^{-1} - 1 \quad (37a)$$

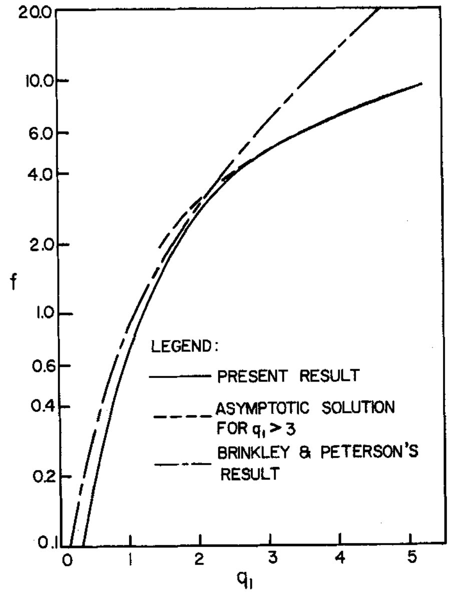


Fig. 1. Comparison of Brinkley and Peterson's result and the result from present analysis for $N_{Nu} \to \infty$, $q_2 = 0$, $R_0 = 1$, and $R_c = 0$.

The corresponding asymptotical form for $q_1 > 3.0$ is

$$f = 2q_1 - 1 \quad (37b)$$

The corresponding functional given by Brinkley and Peterson is, in our notation

$$f = \frac{(6.25 + q_1^2)q_1}{6.25(1 - e^{-q_1})} - 1 \quad \text{for} \quad q_1 > 2.5 \quad (37c)$$

Figure 1 shows a plot of those two f vs. q_1. The two results differ considerably, especially when $q_1 > 2.5$.

THE NONLINEAR SYSTEM

The present analysis may be easily extended to nonlinear systems, such as nonisothermal reactions and nonlinear kinetics, etc. Nevertheless, it should be kept in mind that for nonlinear systems the steady state solution is, in general, not available analytically and must be evaluated numerically.

In this section, we illustrate the analysis for a simple system of a single nonisothermal reaction of general kinetics in a catalytic particle of a general shape. If the single reaction contains N components, it may be easily shown that the concentrations of $N - 1$ components may be expressed in terms of the concentration of a key component, say c_s. Consequently, the rate of change of c_s caused by chemical reaction may be expressed as $g(T_s, c_s)$. Therefore, if D_c is the effective diffusivity of the key component, the steady state equations are

$$D_c \nabla^2 c_s + g(T_s, c_s) = 0 \qquad \mathbf{r}\epsilon V \qquad (38)$$

and

$$D_T \nabla^2 T_s + (\Delta H) g(T_s, c_s) = 0 \qquad \mathbf{r}\epsilon V \qquad (39)$$

The bounday conditions for c_s are simply

$$(\mathbf{n}\cdot\nabla) c_s = 0 \qquad \mathbf{r}\epsilon\Sigma_1 \qquad (38a)$$

and

$$D_c (\mathbf{n}\cdot\nabla) c_s = -h_c (c_s - c_e) \qquad \mathbf{r}\epsilon\Sigma_2 \qquad (38b)$$

The corresponding tracer component equation is

$$\frac{\partial\alpha}{\partial t} = D_c \nabla^2 \alpha + g(T_s, c_s) \frac{\alpha}{c_s}, \quad t > 0, \quad \mathbf{r}\epsilon V \quad (40)$$

with the initial condition

$$\alpha = \mu c_s \qquad t = 0 \qquad \mathbf{r}\epsilon\Omega + \Sigma_1 + \Sigma_2 \qquad (40a)$$

and boundary conditions

$$(\mathbf{n}\cdot\nabla)\alpha = 0 \qquad t > 0, \quad \mathbf{r}\epsilon\Sigma_1 \qquad (40b)$$

and

$$D_c (\mathbf{n}\cdot\nabla)\alpha = -h_c \alpha \qquad t > 0, \quad \mathbf{r}\epsilon\Sigma_2 \qquad (40c)$$

By integrating Equation (40) and conditions (40*b*) and (40*c*) with respect to t from $t = 0$ to $t = \infty$, we obtain

$$-\mu c_s = D_c \nabla^2 \beta + g(T_s, c_s) \frac{\beta}{c_s} \qquad \mathbf{r}\epsilon\Omega \qquad (41)$$

$$(\mathbf{n}\cdot\nabla)\beta = 0 \qquad \mathbf{r}\epsilon\Sigma_1 \qquad (41a)$$

and

$$D_c (\mathbf{n}\cdot\nabla)\beta = -h_c \beta \qquad \mathbf{r}\epsilon\Sigma_2 \qquad (41b)$$

where $\beta = \int_0^\infty \alpha dt$. Multiplying Equation (41) through by c_s and then integrating the resulting equation with respect to **r** over Ω, we get

$$-\mu \int_\Omega c_s^2 \, dV = -h_c \int_{\Sigma_2} c_s \beta dS - D_c \int_\Omega (\nabla c_s) \cdot (\nabla\beta) dV + \int_\Omega g(T_s, c_s) \beta dV \quad (42)$$

after using the divergence theorem and conditions (41*a*) and (41*b*). Next, by multiplying β through Equation (38) and then integrating the resulting equation with respect to $\underset{\sim}{\mathbf{r}}$ over Ω, we obtain

$$-h_c \int_{\Sigma_2} \beta(c_s - c_e)dS - D_c \int_\Omega (\nabla\beta)\cdot(\nabla c_s)dV + \int_\Omega g(T_s, c_s)\, \beta dV = 0 \quad (43)$$

after using the divergence theorem and conditions (38*a*) and (38*b*). Combining Equations (42) and (43), we finally have

$$\int_\Omega c_s^2\, dV = \frac{c_e a}{\mu} \quad (44)$$

where $a \equiv \int_0^\infty \int_{\Sigma_2} h_c\, \alpha dS dt$ is the total amount of the radioactive tracer key component in the collected effluent sample. The right-hand side of Equation (44) is measurable. Therefore, if the left-hand side of Equation (44) is a function of a single unknown parameter we wish to determine, Equation (44) may be used to evaluate such a parameter. If there is more than one parameter to be determined, additional independent sets of experiments are required.

NOTATION

$\mathbf{A}$ = defined as $[\mathbf{a}^{(1)}, \ldots, \mathbf{a}^{(N)}]$

A_i = chemical species i, $(i = 1, 2, \ldots, N)$

$\mathbf{a}, \mathbf{a}^{(i)}$ defined as $-\mathbf{D} \int_{\Sigma_2} (\mathbf{n}\cdot\nabla)\underset{\sim}{\beta} dS$, $(i = 1, 2, \ldots, N)$

c_e defined by $\mathbf{C}_e = c_e\mathbf{I}$, g.-mole/cc.

c_e = external concentration of the key component, g.-mole/cc.

$\mathbf{c}_e$ = external concentration vector

$c_{e,i}$ = external concentration of A_i, $(i = 1, 2)$, g.-mole/cc.

$\mathbf{c}_e^{(i)}$ = $\mathbf{c}_e$ of the i^{th} experiment, $(i = 1, 2, \ldots, N)$

$\mathbf{c}^*$ = equilibrium concentration vector

c_s = concentration of the key component, g.-mole/cc.

$\mathbf{c}_s$ = concentration vector at steady state

$\mathbf{C}_e$ defined as $[\mathbf{c}_e^{(1)}, \ldots, \mathbf{c}_e^{(N)}]$

D defined by $\mathbf{D} = D\mathbf{I}$, sq.cm./sec.

$\mathbf{D}$ = diffusivity matrix, a diagonal matrix

D_c = effective diffusivity of the key component, sq.cm./sec.

D_i = effective diffusivity of A_i, $(i = 1, 2)$, sq.cm./sec.

D_T = thermal diffusivity of the particle, sq.cm./sec.

$\mathbf{E}_{11}$ = matrix with zero elements everywhere except in its first diagonal element, which is unity

f = ratio of the total amount of the radioactive tracer product to the total amount of the radioactive tracer reactant in the effluent sample

F_i defined in Equation (35), $(i = 1, 2)$

G defined as $(\lambda_2 + N_{Nu} \coth \lambda_2)^{-1}$

$g(T_s, c_s)$ = rate of change of c_s due to chemical reaction

$\mathbf{H}$ = mass transfer coefficient matrix, a diagonal matrix

h_c = mass transfer coefficient of the key component, cm./sec.

ΔH = heat of reaction per mole of the key component, (cc.)(°K.)/g.-mole

$\mathbf{I}$ = identity matrix

k_i^j = rate constant of the reaction $A_i \rightarrow A_j$, $(i, j = 1, 2, \ldots, N; i \neq j)$, 1/sec.

$\mathbf{K}$ = reaction rate matrix, defined as

$$\begin{bmatrix} \sum\limits_{j=1}^{N}{}'_1\; k_1^j & -k_2^1 & & -k_N^1 \\ -k_1^2 & \sum\limits_{j=1}^{N}{}'_2\; k_2^j & & -k_N^2 \\ \cdots & \cdots & \cdots & \cdots \\ -k_1^N & -k_2^N & & \sum\limits_{j=1}^{N}{}'_N\; k_N^j \end{bmatrix}$$

L = characteristic length of the particle, cm.

$\mathbf{M}$ defined by Equation (3)

$\mathbf{n}$ = outward normal of Σ

N = total number of chemical species

N_{Nu} defined by $\mathbf{N}_{Nu} = N_{Nu}\mathbf{I}$

$\mathbf{N}_{Nu}$ = mass transfer Nusselt number matrix, defined as $L\mathbf{D}^{-1}\mathbf{H}$

$\mathbf{o}$ = zero vector

$\mathbf{O}$ = zero matrix

$\mathbf{P}$ defined as $(2\pi L^3)^{-1}\mathbf{X}^{-1}\int_\Omega \mathbf{M}^2 dV\, \mathbf{X}$

$(\mathbf{P})_i$ = i^{th} diagonal element of $\mathbf{P}$, $(i = 1, 2, \ldots, N)$

q_1 defined as $L\,(k_1^2/D_1)^{1/2}$

q_2 defined as $L\,(k_2^1/D_2)^{1/2}$

R_0 defined as D_2/D_1

R_c defined as c_{e2}/c_{e1}

r = coordinate of the spherical geometry, cm.

$\mathbf{r}$ = position vector

S = surface area of the particle, sq.cm.

t = time, sec.

V = volume of the particle, cc.

$\mathbf{X}$ = transformation matrix composed of the eigenvectors of $\mathbf{K}$

x = coordinate of the slab geometry, cm.

$\mathbf{Y}$ = transformation matrix composed of the eigenvectors of $\mathbf{D}^{-1}\mathbf{K}$

$\mathbf{1}$ vector whose elements are all unity

$\sum\limits_{j=1}^{N}{}'_i$ sum on $j, j \neq i$

Greek Letters

α = radioactive tracer concentration of the key component, g.-mole/cc.

$\underset{\sim}{\alpha}$ = radioactive tracer concentration vector

β defined as $\int_0^\infty \alpha(\mathbf{r}, t)dt$, (g.-mole)(sec.)/cc.

$\underset{\sim}{\beta}$ = defined as $\int_0^\infty \underset{\sim}{\alpha}(\mathbf{r}, t)dt$

μ = fraction of the radioactive tracer component at steady state, $0 \leqq \mu \leqq 1$

λ_i = diagonal elements of $\underset{\sim}{\Lambda}$, $(i = 1, 2, \ldots, N)$

$\underset{\sim}{\Lambda}$ = diagonal form of $\underset{\sim}{\Phi}$

$\Sigma, \Sigma_1, \Sigma_2$ = surface of the particle

$\underset{\sim}{\Phi}$ defined as $L(\mathbf{D}^{-1}\mathbf{K})^{1/2}$

Ω = interior region of the catalyst

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