# Lumping Nonlinear Kinetics in Porous Catalysts: Diffusion-Reaction Lumping Strategy

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*Nonlinear kinetics in multicomponent mixtures are best described in terms of continuous distribution functions. The quasilinearization procedure that we introduced in 1988 for "uniform" kinetics does not carry over to problems where second-order derivatives appear, as in all cases where diffusion phenomena are of importance. We analyze a simple diffusion-reaction problem in a porous catalyst, by making use of a perturbation technique. The general conclusions reached from this specific problem can be generalized to a wider class of diffusion-reaction problems in complex mixtures.*

## Introduction

The problem of lumping nonlinear chemical kinetics in multicomponents mixtures described as continuous mixtures has received much attention in the recent literature (see, for example, Sapre and Krambeck, 1991; Astarita and Sandler, 1991; Aris and Astarita, 1989). In 1988, we presented an approach based on an assumption of *uniformity* of the kinetic constitutive equation which reduces the problem in a batch reactor (that is, the purely kinetic problem where only first-order derivatives occur) to a quasilinear form which admits analytical solutions for at least some special forms of the relevant distributions.

Aris and Astarita (1989) have remarked that "whether results of this kind can be extended to higher order equations is an open question. There is some incentive to do this from the diffusion and reaction in porous catalysts (Luss and Golikeri, 1971)." This is the problem that we address in this article; the essential aspects of the difficulties to be overcome is discussed below.

When dealing with the batch reactor problem, the assumption of uniformity of Astarita and Ocone (1988) reduces the differential equation to a quasilinear form which can be formally integrated by the introduction of a warped time; we reviewed the technique (1992). The quasilinearity of the problem is crucially related to the fact that only first-order derivatives with respect to time (in a batch reactor), or axial position (in a plug-flow reactor), appear in the balance equations; in fact the quasilinearity carries over to different types of reactors, such as a continuous stirred tank reactor (Astarita and Nigam, 1989), or a maximum mixedness reactor of the Zwietering (1959) type endowed with an arbitrary residence time distribution (Astarita and Ocone, 1990): all such problems involve at most first derivatives or, in the CSTR case, integrals.

However, when one considers problems where chemical kinetics are coupled with diffusion phenomena, as is indeed the case in porous catalysts, *second* derivatives (with respect to spatial position) appear in the balance equations, and the assumption of uniformity does not result in a quasilinear problem at the level of second-order derivatives.

This fundamental difficulty can (at least partially) be circumvented, as will be seen in the body of this article, by a perturbation expansion method. The method is developed here only for the case of a system of catalytic reactions in a porous catalyst, but it should become obvious that in principle the method can be applied to *any* problem where second derivatives appear because of a diffusional contribution to the mass balance equation. In actual fact, in the application of the method, the assumption of uniformity (which is a rather strong one) does not play any crucial role: the case of *nonuniform* nonlinear kinetics can be analyzed with little more algebraic difficulty. We develop a perturbation expansion analysis for both small and large Thiele moduli; these will be shown to result in some results which only in hindsight may be regarded as trivial ones.

## Basic Nomenclature and Definitions

Consider a multicomponent fluid mixture described in a continuous way, so that components are identified by a continuous label $x$ which, without loss of generality, may be assumed to range between 0 and $\infty$. Let $\underline{C}(x, \tau)dx$ (we use underlined symbols to identify dimensional quantities) be the concentration of components with labels between $x$ and $x+dx$ at some condition identified by the value of $\tau$ (the latter could in principle be a vector, but in actual fact we will restrict attention to the case where $\tau$ is a scalar). Let $u$ be the label when interpreted as a dummy variable on integration over its range, and let integrals over the label range be identified with $\langle\,\rangle$:

$$\langle f(u)\rangle = \int_0^\infty f(u)du \tag{1}$$

Concentrations may be normalized as follows. Let $\tau^*$ be some particular value of $\tau$ for which $\langle \underline{C}(u, \tau^*)\rangle = \underline{C}^*$ is known. One may define $g(x, \tau)$ as $\underline{C}(x, \tau)/\underline{C}^*$. The dimensionless "lumped" concentration at $\tau$ is $V(\tau) = \langle \underline{C}(x, \tau)\rangle/\underline{C}^*$, with $V(\tau^*) = 1$.

We now come to kinetics. Let the kinetics in a batch reactor be described as follows:

$$-\partial g(x, \tau)/\partial\tau = xg(x, \tau)F[\langle K(x, u)g(u, \tau)\rangle] \tag{2}$$

Here $\tau$ is identified with the actual time, made dimensionless by multiplying it by the average kinetic constant in the initial mixture, $\underline{k}^*$; the label $x$ has been normalized to be proportional to the kinetic constant of reactant $x$; $F[\,]$ is the nonlinearity factor (the value of which is identically unity for first-order reactions), and the kernel $K(x, u)$ is a yardstick of the influence of the generic reactant $u$ on the rate of consumption of the specific reactant $x$. $\tau^*$ is of course chosen as the initial time, $\tau^* = 0$. The initial concentration distribution $g(x, 0) = G(x)$ is given; the normalizations made imply that both the zeroth and the first moment of $G(x)$ are unity, $\langle G(u)\rangle = \langle uG(u)\rangle = 1$.

In the analysis of the batch reactor problem (that is, of the purely kinetic problem) a very powerful assumption is that of *uniformity*, that is, that the kernel $K(x, u)$ does not depend on $x$, $K(x, u) = K(u)$. It is a very strong assumption, but in fact one which is justified in a variety of realistic cases; it is a powerful assumption in that it makes Eq. 2 a *quasilinear* one, which can be integrated by introducing a warped time (Astarita and Ocone, 1992). This implies that, at least for some simple forms of $G(x)$ and $K(x)$ such as Eqs. 14 and 29, a lumped kinetic function $R(V)$ such that $-dV/d\tau = R(V)$ can be calculated explicitly (Aris and Astarita, 1989). The warped time technique does not apply to higher order differential equations, and it therefore loses usefulness when one considers problems where chemical reactions are coupled with diffusion phenomena. It is the latter class of problems which we attack in this article.

We restrict attention to the simplest problem of coupled diffusion and reaction, namely, the diffusion-reaction phenomenon in a porous catalyst of flat slab geometry. Let $z$ be distance from the exposed surface divided by the slab half-thickness $\underline{L}$, and let $\underline{D}$ be the equivalent diffusivity in the porous catalyst (which, for the sake of simplicity, we assume to be the same for all reactants), and $\underline{k}^*$ the average kinetic constant in the mixture at the exposed surface conditions. The variable $z$ plays the role of $\tau$ in the batch reactor problem. Let $\phi$ be the "lumped Thiele modulus," $\phi^2 = \underline{L}^2\underline{k}^*/\underline{D}$. The concentration distribution in the mixture at the exposed surface is $G(x)$. The differential equation and the boundary conditions of the problem are:

$$g_{zz}(x, z) = \phi^2 xg(x, z)F[\beta(x, z)] \tag{3}$$

$$\beta(x, z) = \langle K(x, u)g(u, z)\rangle \tag{4}$$

$$g(x, 0) = G(x) \tag{5}$$

$$g_z(x, 1) = 0 \tag{6}$$

The assumption that $\underline{D}$ is the same for all components can easily be relaxed. Indeed, suppose that, before rescaling, every component $X$ is characterized by a kinetic constant $\underline{k}(X)$ and a diffusivity $\underline{D}(X)$. One may now rescale the label to $x$ so that $\underline{k}(X)/\underline{D}(X) = \underline{k}^*x/\underline{D}$, and this produces again Eq. 3.

The assumption of uniformity corresponds to setting $\beta(x, z) = \beta(z)$. It is not a powerful assumption in this case, because of the second derivative appearing in Eq. 3. In the following, we first discuss the linear case where $F[\beta]$ is identically unity. We then proceed to the nonlinear case, and we use as a running example that of Langmuir isotherm kinetics, where $F[\beta] = 1/(1+\beta)$.

## Linear Case

In the case of first-order kinetics, $F[\,] = 1$, and $x$ simply plays the role of a parameter in Eq. 3. The solution therefore coincides with the classical one, with $\phi\sqrt{x}$ being the Thiele modulus for component $x$:

$$g(x, z) = G(x)[\cosh(\phi z\sqrt{x}) - tgh(\phi\sqrt{x})\sinh(\phi z\sqrt{x})] \tag{7}$$

Let $\underline{R}(x)$ be the actual total rate of reaction per unit exposed surface of reactant $x$, and $\underline{R}^o(x)$ the value that $\underline{R}(x)$ would have should $g(x, z)$ be $G(x)$ everywhere:

$$\underline{R}(x) = -\underline{k}^*\underline{C}^*\underline{L}\int_0^1 xg(x, z)dz \tag{8}$$

$$\underline{R}^o(x) = \underline{k}^*\underline{C}^*\underline{L}xG(x) \tag{9}$$

The $x$-reactant effectiveness factor, $b(x)$, is of course $\underline{R}(x)/\underline{R}^o(x)$, and this has, as expected, the same form as in the classical case:

$$b(x) = tgh(\phi\sqrt{x})/\phi\sqrt{x} \tag{10}$$

The "lumped" effectiveness factor, $B$, is $\langle \underline{R}(u)\rangle/\langle \underline{R}^o(u)\rangle$. Since $\langle uG(u)\rangle = 1$, one obtains:

$$B = \langle G(u)\sqrt{u}\,tgh(\phi\sqrt{u})\rangle/\phi \tag{11}$$

Two points are of some importance. First, while the individual reactant effectiveness $b(x)$ is given by the same equation one would obtain for a single component with Thiele modulus $\phi\sqrt{x}$, this is not true for the lumped effectiveness $B$ (which, incidentally, *is not* equal to $\langle b(u)\rangle$). The second point has to do with the asymptotic behavior of the lumped effectiveness $B$. When $\phi$ is small (much less than unity), one obtains:

$$B = 1 - \phi^2 \langle u^2 G(u) \rangle /3 + O(\phi^4) \qquad (12)$$

This shows that, to within zero order in $\phi^2$, the classical result $B = 1$ is recovered again (the term of order $\phi^2$ is given here for future reference). However, this is not true in the other limit, where $\phi$ is very large. To within zero order in $1/\phi^2$, one obtains:

$$B = \langle G(u)\sqrt{u} \rangle / \phi \qquad (13)$$

which shows that $B$ is still inversely proportional to $\phi$, but the proportionality constant is not unity. If one uses the classical Gamma distribution for $G(x)$:

$$G(x) = \alpha^{\alpha} x^{\alpha-1} e^{-\alpha x} / \Gamma(\alpha) \qquad (14)$$

one obtains:

$$B\phi = \Gamma(\alpha + 1/2)/\Gamma(\alpha)\sqrt{\alpha} \qquad (15)$$

and the value $B\phi = 1$ is obtained only when $\alpha$ approaches $\infty$, which corresponds to the case where there is only a single reactant, when $G(x) = \delta(x-1)$. The parameter $\alpha$ is required to be positive; even at $\alpha = 1$ (an exponential initial distribution) Eq. 15 gives $B\phi = \Gamma(1.5) = 0.886$ which is not very different from unity. However, at $\alpha$ values less than unity $B\phi$ may become significantly less than unity, and when $\alpha$ approaches zero $B\phi$ approaches $2\Gamma(1.5)\sqrt{\alpha}$. If $G(x)$ is as given by Eq. 14, Eq. 12 becomes $B = 1 - \phi^2(\alpha+1)/3\alpha$, which reduces to the one-component result $B = 1 - \phi^2/3$ in the single component limit; the coefficient $(\alpha+1)/\alpha$ is unity for the single component case, 2 at $\alpha = 1$, and it becomes $1/\alpha$ when $\alpha$ approaches zero.

The physical interpretation of the results given above (that is, that the lumped effectiveness factor is always less than it would be for a single reactant) is as follows. As the value of the parameter $\alpha$ decreases, there is a larger and larger fraction of reactants with a small intrinsic kinetic constant, say reactants which have a low specific Thiele modulus. As one moves inwards into the catalyst, there is a higher and higher relative concentration of these refractory reactants. It follows that the average kinetic constant $\langle ug(u, z) \rangle$ decreases with increasing $z$ more strongly as $\alpha$ decreases, and so does the lumped effectiveness $B$.

Although the results for the lumped effectiveness are not trivial ones, the algebra involved in the solution of the first-order reaction problem is rather trivial. The situation is quite different for nonlinear kinetics, as discussed in the next section.

## Nonlinear Case

### *Small Thiele modulus*

We now consider the general nonlinear case represented by Eqs. 3-6. The warping technique cannot be fruitful, because even if $\beta(x, z) = \beta(z)$, there is no warped distance scale which reduces Eq. 3 to a linear one. We therefore approach the problem by means of a perturbation expansion (Nayfeh, 1973), and we use $\epsilon = \phi^2$ as the perturbation parameter, as suggested by Eq. 12. The expansion, as seen below, is a *regular* one. We write:

$$g(x, z) = g_o(x, z) + \epsilon g_1(x, z) + \ldots \qquad (16)$$

$$\begin{aligned}\beta(x, z) &= \langle K(x, u) g_o(u, z) \rangle + \epsilon \langle K(x, u) g_1(u, z) \rangle + \ldots \\ &= \beta_o(x, z) + \epsilon \beta_1(x, z) + \ldots \qquad (17)\end{aligned}$$

$$\begin{aligned}F[\beta(x, z)] &= F[\beta_o(x, z)] + \epsilon F'[\beta_o(x, z)]\beta_1(x, z) + \ldots \\ &= F_o + \epsilon F_o{}'\beta_1 + \ldots \qquad (18)\end{aligned}$$

In Eq. 18, $F'$ is the ordinary derivative of $F$, which is assumed to be differentiable as many times as needed at $\beta_o(x, z)$. The boundary conditions become:

$$g_o(x, 0) + \epsilon g_1(x, 0) + \ldots = G(x) \qquad (19)$$

$$g_{oz}(x, 1) + \epsilon g_{1z}(x, 1) + \ldots = 0 \qquad (20)$$

The zero-order solution is trivial. Equation 3 implies that $g_{ozz} = 0$, and hence $g_{oz}$ depends only on $x$; Eq. 20 now implies that $g_{oz}$ is identically zero, and hence that $g_o$ depends only on $x$. Hence from Eq. 19:

$$g_o(x, z) = G(x) \qquad (21)$$

This of course implies that, at the zero-order level, both the single component effectiveness and the lumped effectiveness are unity, as expected. Notice that $\beta_o(x, z) = \langle K(x, u) G(u) \rangle$ is in fact independent of $z$, and that therefore the assumption of differentiability for $F[\,]$ is milder than it may appear at first sight. It is also important to note that $F_o$ is of course also independent of $z$, and so are $F_o{}'$, $F_o{}''$, …, which are all functions of only $x$. In the case of uniform kinetics, $F_o$, $F_o{}'$, .. are in fact constants.

At the first-order level, the differential equation becomes:

$$g_{1zz} = xG(x)F_o \qquad (22)$$

Taking into account the boundary condition of Eq. 20, this integrates to:

$$-g_{1z}(x, z) = xG(x)F_o(1 - z) \qquad (23)$$

Taking into account the boundary condition of Eq. 19, this integrates to:

$$g_1(x, z) = -xG(x)F_o(z - z^2/2) \qquad (24)$$

The dimensionless total rate of reaction per unit exposed surface, $R(x) = \underline{R}(x)/\underline{k}^* \underline{C}^* \underline{L}$, and its reference value $R^o(x)$, are obtained as:

$$\begin{aligned}R(x) = xG(x)F_o(x) &- \epsilon[x^2 G(x) F_o^2(x) \\ &+ xG(x)F_o{}'(x)\langle K(x, u) u G(u) F_o(u) \rangle]/3 \qquad (25)\end{aligned}$$

$$R^o(x) = xG(x)F_o(x) \qquad (26)$$

The individual reactant effectiveness is, to within $O(\epsilon^2)$:

$$\begin{aligned}b(x) = 1 &- \epsilon[xF_o(x) \\ &+ F_o{}'(x)\langle K(x, u) u G(u) F_o(u) \rangle / F_o(x)]/3 \qquad (27)\end{aligned}$$

Since $R(x)$ contains an integral, as shown in Eq. 25, the lumped effectiveness, at the first-order level, will contain two nested integrals; the algebra, although straightforward, soon becomes rather tedious and the results not very illuminating. Some significant simplification, however, does arise in the case of uniform kinetics, where $F_o$ and its derivatives are constants. This simplifies the algebra significantly, and the lumped effectiveness is obtained to within $O(\epsilon^2)$ without any nested integrals:

$$B = 1 - \epsilon[F_o' \langle K(u)uG(u)\rangle + F_o\langle u^2G(u)\rangle]/3 \qquad (28)$$

This allows a simple check by comparison with Eq. 12. The linear case is of course uniform, $F_o = 1$ and $F_o' = 0$, so that Eq. 12 is correctly recovered.

The interesting point about Eq. 28 is that the term in square brackets may well be negative, so that the (isothermal) lumped effectiveness may in fact be larger than unity at moderately small Thiele moduli. In order to clarify this point, we choose the gamma distribution for $G(x)$, and the distribution proposed by Astarita (1989) for $K(x)$:

$$K(x) = K^*(\alpha x)^\sigma \Gamma(\alpha)/\Gamma(\alpha+\sigma) \qquad (29)$$

where $K^*$ is the average value of $K(x)$ in the mixture at the exposed surface; the parameter $\sigma$ is subject to $\alpha+\sigma>0$. Equation 28 reduces to:

$$B = 1 - \epsilon[F_o' K^*(\alpha+\sigma)/\alpha + F_o(\alpha+1)/\alpha] \qquad (30)$$

This may well be larger than unity if $F_o'$ is negative, and its absolute value larger than $F_o(\alpha+1)/K^*(\alpha+\sigma)$. The point is best illustrated by considering the Langmuir isotherm kinetics form of the $F[\,]$ function, for which indeed $F_o'$ is negative:

$$F_o = 1/(1+K^*) \qquad (32)$$

$$F_o' = -1/(1+K^*)^2 \qquad (33)$$

If $\sigma$ is less than unity, $B$ as given by Eq. 30 will be no larger than unity. However, if $\sigma$ is larger than unity, $B$ will be larger than unity if:

$$K^* > (\alpha+1)/(\sigma-1) \qquad (34)$$

The batch reactor performance of the lumped behavior of the Langmuir isotherm kinetics case has been analyzed by Astarita (1989); the lumped kinetic function is $R(V) = V^{(\alpha+1)/\alpha}/[1+K^* V^{(\alpha+\sigma)/\alpha}]$. The derivative $R'(1)$ is negative (that is, the apparent overall order of reduction is negative at the initial concentration distribution) if the condition in Eq. 34 is satisfied. The physical reason for this is that, when $\sigma>1$, reactants with large kinetic constant also adsorb strongly on the catalytic surface, and the latter effect predominates: as the fast reacting components disappear, the catalyst surface becomes more available, and the average rate of reaction in fact increases. This explains the physics of the result obtained: to within order zero in $\epsilon$, the concentration distribution is $G(x)$ (as it is at $V=1$ in the batch reactor case), and a lumped effectiveness larger than unity is predicted to within first order in $\epsilon$ because the apparent lumped order of reaction is negative at that distribution.

### *Large Thiele modulus*

We now consider the case where the lumped Thiele modulus is large, $\phi \gg 1$, and we perform again a perturbation expansion. The perturbation parameter is now $1/\phi^2$, and the perturbation is immediately recognized as a *singular* one: the coefficient of the highest order derivative goes to zero. The "outer" solution is trivially obtained as $g(x, z) = 0$, which satisfies the differential Eq. 3 and the boundary condition in Eq. 6, but *does not* satisfy the boundary condition in Eq. 5. The "inner" solution is to be sought from Eq. 3, and a "stretched coordinate" $y$ is to be determined which makes the left-hand side of the same order of magnitude as the right-hand one. Since $x$ plays the role of a parameter in Eq. 3, the stretched coordinate definition may well include $x$, and in fact the following definition suggests itself naturally:

$$y = \phi z\sqrt{x} \qquad (35)$$

It is now natural to define the following quantities:

$$q(x, z) = g(x, z)/G(x) \qquad (36)$$

$$p(x, u) = K(x, u)G(u) \qquad (37)$$

so that:

$$\beta(x, z) = \langle p(x, u)q(u, z)\rangle \qquad (38)$$

With this, the differential equation and boundary conditions become as follows (with Eq. 41 being the classical "stretched coordinate" boundary condition, which requires the limit of the inner solution as the stretched coordinate approaches $\infty$ to coincide with the limit of the outer solution when the unstretched coordinate approaches zero):

$$q_{yy}(x, y) = q(x, y)F[\langle p(x, u)q(u, y)\rangle] \qquad (39)$$

$$q(x, 0) = 1 \qquad (40)$$

$$q(x, \infty) = 0 \qquad (41)$$

Expansion of the inner problem does not yield any advantage, because all solutions except the first-order one are identically zero, and the first-order one is governed by the complete set of Eqs. 39-41. However, some property of the solution can be inferred by the following argument. Let boldface symbols identify functionals (Riesz and Nagy, 1955) of functions defined over the label range, with $v$ the dummy component label variable when a function of it is the argument of a functional. The solution of Eqs. 39-41 is necessarily of the following form:

$$q(x, y) = \mathbf{Q}[p(x, v); y] \qquad (42)$$

where $\mathbf{Q}[;]$ is a functional of $p(x, v)$ which depends parametrically on $y$ (and, of course, on $x$ as well, except in the uniform case).

For future (rather transparent) reference, it is useful to have an expression for the gradient of $q(\ )$ at the exposed surface $y=0$; this is simply $Q_y[x, 0]$ which does not depend on $y$:

$$-q_y(x, 0)=P[p(x, v)] \tag{43}$$

If one integrates Eq. 3 between $z=0$ and $z=1$, taking into account the boundary conditions, one obtains:

$$-g_z(x, 0)=\phi^2\int_0^1 xg(x, z)F[\beta(x, z)]dz=\phi^2R(x) \tag{44}$$

so that, after algebraic manipulation, one obtains:

$$R(x)=x^{1/2}G(x)P[p(x, v)]/\phi \tag{45}$$

while:

$$R^o(x)=xG(x)F[\langle p(x, u)\rangle] \tag{46}$$

Thus one obtains:

$$b(x)=P[p(x, v)]/\phi\sqrt{x}F[\langle p(x, u)\rangle] \tag{47}$$

$$B=\langle x^{1/2}G(x)P[p(x, v)]\rangle/\phi\langle xG(x)F[\langle p(x, u)\rangle]\rangle \tag{48}$$

The important points to note here are that both the individual reactant effectiveness factor $b(x)$, and the lumped effectiveness $B$, are inversely proportional to $\phi$, no matter what the nonlinear function $F[\ ]$ might be, and secondly, that the lumped effectiveness factor involves a nested integral.

Some simplification occurs in the case of uniform kinetics. Since $p(x, v)=p(v)$, the right-hand side of Eq. 43 becomes a constant (for any assigned $G(x)$ distribution), say:

$$P[p(v)]=P[K(v)G(v)]=P \tag{49}$$

Furthermore, $F[\langle p(v)\rangle]=F[K^*]$, and hence one obtains:

$$b(x)=P/F[K^*]\phi\sqrt{x} \tag{50}$$

$$B=P\langle x^{1/2}G(x)\rangle/\phi F[K^*] \tag{51}$$

Equation 50 shows that the individual reactant effectiveness factor is inversely proportional to the individual Thiele modulus $\phi\sqrt{x}$, though the proportionality constant is not the same as one would have in the case of a single reactant, since the value of $P$ depends on the whole spectrum of concentrations. In particular, if $G(x)$ is a gamma distribution, $P$ depends on the parameter $\alpha$, $P=P(\alpha)$, and its value when $\alpha$ tends to $\infty$ is the value one would calculate for the same kinetics in the case of a single component. We have been unable to find an analytical approximation of the functionals $P[\ ]$ and $Q[\ ]$ (except for a purely formal solution discussed in the Appendix). Therefore we cannot go beyond these results in the analysis of the high Thiele modulus asymptote.

## Conclusions

We have analyzed the lumping strategy for nonlinear kinetics in continuous mixtures when diffusion effects are present in addition to the chemical reactions. Our analysis has been restricted to the simplest possible problem in this category, namely, reaction-diffusion in a porous catalyst of flat slab geometry. However, some of the conclusions which have been reached are clearly of a rather general nature; here we briefly review these.

(1) Although the assumption of uniform kinetics does not make the diffusion-reaction problem a quasilinear one, it still simplifies the algebra involved to a considerable degree.

(2) In the limit of large diffusivities, a perturbation expansion procedure (which is a regular one) produces some significant results. The algebra becomes quite cumbersome at any level of perturbation beyond the zero- and first-order ones. The assumption of uniformity simplifies very significantly, but not crucially, the algebra involved. The lumped selectivity in isothermal systems at moderately small Thiele moduli may become larger than unity when the apparent overall order of reaction at the exposed surface conditions is negative.

(3) In the limit of small diffusivities, the perturbation procedure is a singular one. It follows that only some general properties of the solution can be inferred, unless the zero-order problem for the inner solution is one which can be solved formally. This is not the case for heterogeneous catalysis, but it would in fact be the case in a plug-flow reactor with axial diffusion under the assumption of uniformity.

## Notation

$b(\ )$ = individual effectiveness factor
$B$ = lumped effectiveness factor
$\underline{C}$ = concentration of individual component, kmol/m$^3$
$\underline{D}$ = diffusivity, m$^2$/s
$F[\ ]$ = nonlinearity factor
$F'$ = derivative of $F$
$G(\ )$ = exposed surface concentration distribution
$g(\ )$ = dimensionless concentration distribution
$h(\ )$ = inverse concentration function
$H[\ ]$ = function defined in Eq. A4
$K$ = value of $K(\ )$ for single reactant case
$K(\ )$ = interaction parameter distribution
$K^*$ = average value of $K()$ at $G(x)$
$k^*$ = average kinetic constant, s$^{-1}$
$\underline{L}$ = catalyst halfthickness, m
$p(\ )$ = defined in Eq. 37
$P$ = value of $P[\ ]$ in uniform case
$P[\ ]$ = functional defined in Eq. 43
$q(\ )$ = defined in Eq. 36
$Q[\ ]$ = functional defined in Eq. 42
$R(\ )$ = dimensionless overall reaction rate
$\underline{R}(\ )$ = reaction rate per unit exposed surface, kmol/m$^2\cdot$s
$R^o(\ )$ = dimensionless reference reaction rate
$\underline{R}^o(\ )$ = reference reaction rate, kmol/m$^2\cdot$s
$\overline{S}(\ )$ = lumped kinetic function
$u$ = component label, when dummy under integration
$V$ = dimensionless lumped concentration
$v$ = dummy component label when subargument of a functional
$X$ = component label
$x$ = rescaled component label
$y$ = stretched coordinate
$z$ = dimensionless coordinate

### Greek letters

$\alpha$ = parameter in $G(x)$ distribution
$\beta(\ )$ = defined in Eq. 4
$\Gamma(\ )$ = gamma function or generalized factorial
$\epsilon$ = perturbation parameter, $=\phi^2$
$\sigma$ = parameter in $K(\ )$ distribution
$\tau$ = parameter identifying local conditions
$\phi$ = Thiele modulus

### Operators

$\langle\ \rangle$ = integral over range of $x$
boldface = a functional

### Subscripts

letters = partial derivative
integers = order of expansion

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## Appendix

Consider the high Thiele modulus asymptote for the case of a single component (which is uniform by definition). Let $y$ be defined as in Eq. 35 (with $x=1$ by default), and let $c(y)$ be the single component equivalent of $q(x, y)$, and $K=K(1)$. The solution is trivially obtained as (with $w$ the concentration $c$ when appearing as a dummy variable):

$$P = -c_y(0) = \left[2\int_0^1 wF[Kw]dw\right]^{1/2} \qquad \text{(A1)}$$

Hence, the effectiveness factor, $P/\phi F[K]$, can be calculated by quadrature. For instance, in the Langmuir isotherm kinetics case, $F(Kw) = 1/(1+Kw)$, and one obtains:

$$b = [2(1+K)/K^2][K - \ln(1+K)]/\phi \qquad \text{(A2)}$$

which yields the correct result $b = 1/\phi$ for $K$ approaching zero.

The classical procedure to obtain the result in Eq. A1 (which is all that is needed in order to calculate the effectiveness factor) is based on the assumption that the $c(y)$ function is *invertible*, that is, it is monotonous. The physics of the problem guarantee this, and therefore the result is of a general nature.

If one tries to apply the same procedure to Eqs. 39-41, one first needs to assume that $q(x, y)$ is invertible for any $x$, which again is (presumably) guaranteed by the physics of the problem, because $q_y$ is negative. Hence an inverse function $h(\ )$ exists such that:

$$y = h(x, q) \qquad \text{(A3)}$$

Thus, at least formally, one may write:

$$F[\langle p(x, u)q(u, y)\rangle] = F[x, y] = F[x, h(x, q)] = H(x, q) \qquad \text{(A4)}$$

This leads, formally, to a solution of the problem, since one obtains (with $w$ the value of $q$ when appearing as a dummy variable):

$$-q_y(0) = \left[2\int_0^1 xwH[x, w]dw\right]^{1/2} \qquad \text{(A5)}$$

However, $H[x, q]$ is now delivered by a horrendous integro-differential equation, which is in turn based on the slightly less horrendous one for $h(x, q)$:

$$-h_q = \left[2\int_0^q xwH[x, w]dw\right]^{-1/2} \qquad \text{(A6)}$$

$$h(x, 1) = 0 \qquad \text{(A7)}$$

We have been unable to imagine *any* case (except the trivial one where $F[\,]$ is identically unity) for which this route leads to an explicit solution.

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